

Quantum mechanical reactive scattering for planar atom plus diatom systems. I. Theory*

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A method is presented for accurately solving the Schrödinger equation for the reactive collision of an atom with a diatomic molecule on a space-fixed plane. The procedure consists primarily of two steps. First, the Schrödinger equation in each of the three arrangement channel regions is transformed into a set of coupled differential equations and numerically integrated in each of these regions to generate primitive solutions. The rotational part of the vibration-rotation basis functions involved is not changed from its asymptotic form during this propagation, but the vibrational eigenfunctions as well as the integration variable are changed periodically so as to follow the vibrational motions in a nearly adiabatic manner. In the second step, the primitive solutions generated in each of the three arrangement channels are smoothly matched to each other on a set of appropriately chosen matching surfaces. The resulting solutions are then linearly combined to satisfy the proper asymptotic boundary conditions, and the scattering matrix, scattering amplitudes, and cross sections are determined. Application of this procedure to the special case of the $H+H_2$ reaction is discussed in detail including simplifications arising from the additional symmetries involved, and the inclusion of effects resulting from indistinguishability of identical particles.

I. INTRODUCTION

In recent years, much interest has developed in the *ab initio* calculation of bimolecular reaction cross sections on realistic potential energy surfaces by accurate quantum mechanical techniques. The motivation for such calculations has been to interpret the results of crossed molecular beam experiments, to understand the effect of the relative translational energy of the reactants and of their internal state on such cross sections and on the disposal of energy among the reaction products, to elucidate the role of direct and compound state dynamical mechanisms, to test the range and degree of validity of approximate reaction models (such as the adiabatic and statistical ones), to develop new physical models of known reliability, to examine the correctness of the dynamical assumptions of transition state theory, to establish the conditions of applicability of the quasi-classical trajectory calculations and of semiclassical improvements thereof, and last, but not least, to make detailed qualitative and quantitative predictions from first principles about reactions difficult to investigate experimentally.

Owing in part to the lack of appropriate numerical techniques and to limitations of the memory size and computational speed and cost of present-day large computers, most of these quantum calculations so far have been performed for collinear atom-diatom reactions.¹⁻¹³ In recent years, several attempts have been made to do calculations for nonlinear triatomic systems. Saxon and Light¹⁴ and Altenberger-Siczek and Light¹⁵ have investigated the coplanar $H+H_2$ exchange reaction by a coupled-channel technique which excluded closed vibrational channels. Wolken and Karplus¹⁶ have made a study of this same reaction in three dimensions, also ignoring closed vibrational channels. Wyatt and co-workers¹⁷ have developed techniques which include closed vibrations in calculations on one and two reaction path atom plus diatom reactions, and Elkowitz and Wyatt^{17a} have applied these methods to the three-dimensional $H+H_2$ reaction. Baer and Kouri¹⁸ have done fully

converged calculations in three dimensions on a model (one reaction path) triatomic system in which one of the atoms was assumed infinitely heavy and in which the simple potential used allowed a partially analytic treatment.

In an earlier communication,¹⁹ we presented preliminary results of the first fully converged quantum mechanical calculation for a coplanar reaction on a realistic electronically adiabatic potential energy surface, that for $H+H_2$. These results indicated that the quantitative differences between calculations in which closed vibrations are included and those for which they are not can be quite serious. In this paper, we will present a detailed description of the method used to perform such calculations. We will formulate the method for a general atom plus diatomic molecule collision on a single reactive potential energy surface using $H+H_2$ as a specific example. A detailed description of the results of our extensive calculations on coplanar $H+H_2$ will be given elsewhere.²⁰

The method is based on an earlier coupled-channel (i.e., close-coupling) propagation technique⁵ which has been extensively applied to the collinear $H+H_2$ and $F+H_2$ reactions.¹⁰ The spirit of the collinear method is to choose different variables and different pseudovibrational basis functions for expansion of the solutions of the Schrödinger equation in different local regions of the (collinear) configuration space so as to minimize the number of terms needed for accurate convergence of the expansions. This concept is retained for the vibrational motion in our application of the method to coplanar collisions. However, the variables and basis functions describing rotational motion are not changed (and hence retain their asymptotic meanings) during the integration into the interaction region from each of the three separated arrangement channel regions of internal configuration space. As a result, an additional step is required at the completion of the integration in which the primitive solutions in each of the three arrangement channel regions are smoothly matched to each other on a set of

three appropriately chosen surfaces which separate these three regions.²¹ The restriction that the three atoms should be confined to a space-fixed plane was introduced for computational convenience to test out the effectiveness of the method without excessive expenditure of computation time. Extension to reactions in three-dimensional space is reasonably straightforward and has recently been implemented by Kuppermann and Schatz²² for 3D $H + H_2$ in the first fully converged quantum mechanical treatment of a chemical reaction on a realistic potential energy surface.

In Sec. II of this paper we formulate the Schrödinger equation for the problem and describe the partial wave expansion used to obtain the partial differential equations, in internal configuration coordinates, which must be solved. The method used to integrate these equations in the different regions of configuration space is described in Sec. III, and in Sec. IV we describe how we smoothly match the solutions obtained from these integrations. The asymptotic analysis is developed in Sec. V, including the methods of calculating the reactance and scattering matrices, the scattering amplitudes, and the cross sections. Finally, in Sec. VI we describe the simplifications and changes involved in an application of the method to the $H + H_2$ exchange reaction due to the identity of the three atoms, including a discussion of the technique of antisymmetrizing the scattering wavefunction (post antisymmetrization) in a way which is applicable to the three-dimensional case also.

II. FORMULATION OF THE PROBLEM

A. General considerations

We are interested in calculating cross sections for the exchange reaction $A + BC \rightarrow AB + C$, $AC + B$ in which the three atoms A, B, and C are confined to remain on a space-fixed plane. We assume that the Born-Oppenheimer separation approximation between the electron and nuclear motions is valid and that the resulting ground electronic state potential energy surface V is known. We further assume that all higher potential energy surfaces are sufficiently greater than the total energy E of the system everywhere in configuration space for us to be able to neglect their influence on the cross sections. This "single potential energy surface" model is applicable to a high degree of accuracy to many triatomic reactions. We also assume that E is sufficiently low for the existence and effect of break-up collisions of the type $A + BC \rightarrow A + B + C$ to be negligible. Finally, we assume that the interactions between the nuclear spin and nuclear orbital angular momenta are negligible.

Let \mathbf{r}_A , \mathbf{r}_B , and \mathbf{r}_C be the position vectors of nuclei A, B, and C, respectively, with respect to their center of mass. We wish to obtain a solution to the time-independent Schrödinger equation for the motion of the nuclei which satisfies the following three conditions:

- In configuration space \mathbf{r}_A , \mathbf{r}_B , \mathbf{r}_C it is everywhere single valued and continuous and has gradients which are everywhere continuous (except at points in that space for which two of the three atoms coincide).
- It is antisymmetric (symmetric) with respect to

exchange of the space and spin coordinates of any two identical nuclei of half odd-integral (integral) nuclear spin.

- It satisfies the asymptotic conditions describing the collision phenomenon under consideration, i.e., the collision of A and BC with a given relative kinetic energy and a given initial internal quantum state of BC, to produce receding products $A + BC$, $AB + C$, or $AC + B$ in all possible internal states of the diatom compatible with the total energy of the system.

If we can find a sufficient number of independent solutions satisfying Condition (a), it is possible to obtain linear combinations of them which, in addition, satisfy Conditions (b) (by postantisymmetrization methods²³) and (c) (by reactance or scattering matrix analysis techniques²⁴).

B. The Schrödinger equation

Let $\bar{\mathbf{R}}_\alpha$ be the position vector of A with respect to the center of mass of BC and $\bar{\mathbf{r}}_\alpha$ the position vector of C with respect to B, as indicated in Fig. 1. As $\bar{\mathbf{R}}_\alpha \rightarrow \infty$ with $\bar{\mathbf{r}}_\alpha$ remaining finite, we denote the corresponding configuration as arrangement channel $\alpha \equiv (A, BC)$. Let $(\bar{r}_\alpha, \theta_\alpha)$ and $(\bar{R}_\alpha, \theta_\alpha)$ be, respectively, the planar polar coordinates of $\bar{\mathbf{r}}_\alpha$ and $\bar{\mathbf{R}}_\alpha$ with respect to a fixed system of reference attached to the plane (all angles being measured from the Ox axis of Fig. 1). The reduced mass associated to the motion of C with respect to B is denoted by μ_{BC} and that associated to atom A with respect to molecule BC is $\mu_{\alpha, BC}$. We define analogous vectors $\bar{\mathbf{r}}_\beta$, $\bar{\mathbf{R}}_\beta$ and $\bar{\mathbf{r}}_\gamma$, $\bar{\mathbf{R}}_\gamma$ (Fig. 1) and associated coordinates and reduced masses so that as $\bar{\mathbf{R}}_\beta \rightarrow \infty$ or $\bar{\mathbf{R}}_\gamma \rightarrow \infty$ with $\bar{\mathbf{r}}_\beta$ or $\bar{\mathbf{r}}_\gamma$ finite, we obtain the arrangement channels $\beta \equiv (B, CA)$ and $\gamma \equiv (C, AB)$, respectively. Note that the directions of the vectors in Fig. 1 are defined in a cyclic manner in the indices $\alpha\beta\gamma$. Finally, let $\lambda\nu\kappa$ represent any one of the three possible cyclic permutations $\alpha\beta\gamma$, $\beta\gamma\alpha$, and $\gamma\alpha\beta$.

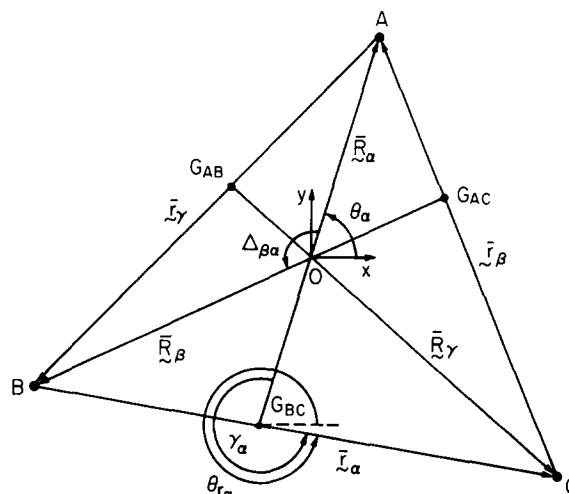


FIG. 1. Vectors used to specify the location of three atoms in the A, B, C collision system relative to the center of mass O. G_{BC} , G_{AC} , and G_{AB} denote the locations of the centers of mass of the diatomic, BC, AC, and AB, respectively. $\bar{\mathbf{R}}_\alpha$, $\bar{\mathbf{r}}_\alpha$, $\bar{\mathbf{R}}_\beta$, $\bar{\mathbf{r}}_\beta$, $\bar{\mathbf{R}}_\gamma$, $\bar{\mathbf{r}}_\gamma$ are defined in text.

In the system of coordinates characterized by index λ ($= \alpha, \beta$ or γ), the Schrödinger equation describing the internal motion of the three-particle system is

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu_{\nu\kappa}} \left(\frac{1}{\bar{r}_\lambda} \frac{\partial}{\partial \bar{r}_\lambda} \bar{r}_\lambda \frac{\partial}{\partial \bar{r}_\lambda} + \frac{1}{\bar{r}_\lambda^2} \frac{\partial^2}{\partial \theta_\lambda^2} \right) \right. \\ & \quad \left. - \frac{\hbar^2}{2\mu_{\lambda\nu\kappa}} \left(\frac{1}{\bar{R}_\lambda} \frac{\partial}{\partial \bar{R}_\lambda} \bar{R}_\lambda \frac{\partial}{\partial \bar{R}_\lambda} + \frac{1}{\bar{R}_\lambda^2} \frac{\partial^2}{\partial \theta_\lambda^2} \right) \right. \\ & \quad \left. + V^\lambda(\bar{r}_\lambda, \bar{R}_\lambda, \gamma_\lambda) - E \right] \Psi^\lambda(\bar{r}_\lambda, \bar{R}_\lambda, \theta_\lambda, \gamma_\lambda) = 0, \quad (2.1) \end{aligned}$$

where V^λ is the potential energy function of the system expressed in λ coordinates, and E is its total energy. γ_λ is by definition the counterclockwise angle from \bar{R}_λ to \bar{r}_λ . It lies in the 0 to 2π range and is equal to $\theta_{r_\lambda} - \theta_\lambda$ modulo 2π . In the absence of external fields, the potential function depends only on the internal variables $\bar{R}_\lambda, \bar{r}_\lambda, \gamma_\lambda$ and satisfies the relation $V^\lambda(\bar{R}_\lambda, \bar{r}_\lambda, \gamma_\lambda) = V^\lambda(\bar{R}_\lambda, \bar{r}_\lambda, 2\pi - \gamma_\lambda)$.

Let us now introduce a set of coordinates used previously by Delves,²⁵ Jepsen and Hirschfelder,²⁶ and Smith.²⁷ They have the advantage of leading to an equation containing a single effective mass μ which is independent of the arrangement channel λ ; this simplifies many of the equations presented below. These coordinates are

$$\mathbf{r}_\lambda = a_\lambda^{-1} \bar{\mathbf{r}}_\lambda, \quad (2.2a)$$

$$\mathbf{R}_\lambda = a_\lambda \bar{\mathbf{R}}_\lambda, \quad (2.2b)$$

where a_λ is a dimensionless scaling constant defined by

$$a_\lambda = (\mu_{\lambda\nu\kappa} / \mu_{\nu\kappa})^{1/4}. \quad (2.3)$$

Substitution into Eq. (2.1) leads to

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu} \left(\frac{1}{r_\lambda} \frac{\partial}{\partial r_\lambda} r_\lambda \frac{\partial}{\partial r_\lambda} + \frac{1}{r_\lambda^2} \frac{\partial^2}{\partial \theta_\lambda^2} + \frac{1}{R_\lambda} \frac{\partial}{\partial R_\lambda} R_\lambda \frac{\partial}{\partial R_\lambda} + \frac{1}{R_\lambda^2} \frac{\partial^2}{\partial \gamma_\lambda^2} \right) \right. \\ & \quad \left. + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - E \right] \Psi^\lambda(r_\lambda, R_\lambda, \theta_\lambda, \gamma_\lambda) = 0, \quad (2.4) \end{aligned}$$

where the circular polar angles of $\mathbf{R}_\lambda, \mathbf{r}_\lambda$ are the same as those of $\bar{\mathbf{R}}_\lambda, \bar{\mathbf{r}}_\lambda$, and μ is the effective mass alluded to above and defined by

$$\mu = (\mu_{\nu\kappa} \mu_{\lambda\nu\kappa})^{1/2} = (m_\alpha m_\beta m_\gamma / M)^{1/2}, \quad (2.5)$$

where

$$M = m_\alpha + m_\beta + m_\gamma$$

is the total mass of the system, and m_α, m_β , and m_γ are the masses of atoms A, B, and C, respectively. We now change from the angular variables $\theta_{r_\lambda}, \theta_\lambda$ to $\gamma_\lambda, \theta_\lambda$, obtaining the following expression from Eq. (2.4):

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r_\lambda} \frac{\partial}{\partial r_\lambda} r_\lambda \frac{\partial}{\partial r_\lambda} + \frac{1}{r_\lambda^2} \frac{\partial^2}{\partial \gamma_\lambda^2} + \frac{1}{R_\lambda} \frac{\partial}{\partial R_\lambda} R_\lambda \frac{\partial}{\partial R_\lambda} \right. \right. \\ & \quad \left. \left. + \frac{1}{R_\lambda^2} \left(\frac{\partial^2}{\partial \theta_\lambda^2} - 2 \frac{\partial^2}{\partial \theta_\lambda \partial \gamma_\lambda} + \frac{\partial^2}{\partial \gamma_\lambda^2} \right) \right] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) \right. \\ & \quad \left. - E \right\} \Psi^\lambda(r_\lambda, R_\lambda, \gamma_\lambda, \theta_\lambda) = 0. \quad (2.6) \end{aligned}$$

This is called the body-fixed Schrödinger equation, because γ_λ is the angle of \mathbf{r}_λ with respect to the body-fixed

\mathbf{R}_λ direction rather than the laboratory-fixed Ox axis. Similarly, $R_\lambda, \theta_\lambda, r_\lambda, \gamma_\lambda$ are called the body-fixed λ coordinates. The independence of V^λ on θ_λ in the above equation introduces very convenient simplifications, as is shown in the next section.

C. Partial wave expansion

The total angular momentum \mathbf{J} of the triatomic system (with respect to its center of mass) is a constant of the motion which commutes with the Hamiltonian H . The solution of the Schrödinger equation we are seeking, satisfying Conditions (a), (b), and (c) of Sec. II. A, is not an eigenfunction of \mathbf{J} .²⁸ It is, however, convenient to perform the coplanar analog of partial wave analysis by expanding Ψ^λ in terms of the simultaneous eigenfunctions Ψ_J^λ of H and \mathbf{J} .

In the system of coordinates $r_\lambda, R_\lambda, \theta_{r_\lambda}, \theta_\lambda$ the operator \mathbf{J} is given by

$$\mathbf{J} = \left[\frac{\hbar}{i} \left(\frac{\partial}{\partial \theta_\lambda} \right)_{\theta_{r_\lambda}} + \frac{\hbar}{i} \left(\frac{\partial}{\partial \theta_{r_\lambda}} \right)_{\theta_\lambda} \right] \hat{\mathbf{z}} \quad \lambda = \alpha, \beta, \gamma, \quad (2.7)$$

where $\hat{\mathbf{z}}$ is the unit vector perpendicular to the fixed plane of motion of the three particles. We recognize from Eq. (2.7) that \mathbf{J} is the algebraic sum of the rotational angular momentum $\mathbf{j}_\lambda = (\hbar/i)(\partial/\partial \theta_{r_\lambda})_{\theta_\lambda} \hat{\mathbf{z}}$ and the orbital angular momentum $\mathbf{l}_\lambda = (\hbar/i)(\partial/\partial \theta_\lambda)_{\theta_{r_\lambda}} \hat{\mathbf{z}}$. Transforming \mathbf{J} to the angular variables $\theta_\lambda, \gamma_\lambda$, we get

$$\mathbf{J} = \frac{\hbar}{i} \left(\frac{\partial}{\partial \theta_\lambda} \right)_{\gamma_\lambda} \hat{\mathbf{z}} \quad \lambda = \alpha, \beta, \gamma, \quad (2.8)$$

which may be physically interpreted as indicating that if γ_λ is maintained constant, a variation of the angular coordinate θ_λ of \mathbf{R}_λ produces a rotation of the entire triatomic system.

The orthonormal eigenfunctions of \mathbf{J} are given by²⁹

$$\varphi_J(\theta_\lambda) = (2\pi)^{-1/2} \exp(iJ\theta_\lambda) \quad J = 0, \pm 1, \pm 2, \dots \quad (2.9)$$

The simultaneous eigenfunctions of H with energy E and of \mathbf{J} with total angular momentum $J\hbar$ are of the form

$$\Psi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda, \theta_\lambda) = \varphi_J(\theta_\lambda) \chi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda), \quad (2.10)$$

where

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r_\lambda} \frac{\partial}{\partial r_\lambda} r_\lambda \frac{\partial}{\partial r_\lambda} + \frac{1}{r_\lambda^2} \frac{\partial^2}{\partial \gamma_\lambda^2} + \frac{1}{R_\lambda} \frac{\partial}{\partial R_\lambda} R_\lambda \frac{\partial}{\partial R_\lambda} \right. \right. \\ & \quad \left. \left. + \frac{1}{R_\lambda^2} \left(-J^2 - 2iJ \frac{\partial}{\partial \gamma_\lambda} + \frac{\partial^2}{\partial \gamma_\lambda^2} \right) \right] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) \right. \\ & \quad \left. - E \right\} \chi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = 0. \quad (2.11) \end{aligned}$$

Any solution Ψ^λ of the Schrödinger equation which is not necessarily an eigenfunction of \mathbf{J} can be written as

$$\Psi^\lambda(r_\lambda, R_\lambda, \gamma_\lambda, \theta_\lambda) = \sum_{J=-\infty}^{\infty} C_J^\lambda \Psi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda, \theta_\lambda). \quad (2.12)$$

The constant coefficients C_J^λ appropriate for the problem being considered will be determined by the asymptotic conditions specified in Requirement (c) of Sec. II. A and will be discussed in Sec. V. B.

We now simplify Eq. (2.11) by defining a new function ψ_J^λ by

$$\psi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = (r_\lambda R_\lambda)^{1/2} \chi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda). \quad (2.13)$$

Substituting this into Eq. (2.11), we obtain

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial r_\lambda^2} + \frac{\partial^2}{\partial R_\lambda^2} + \frac{1}{r_\lambda^2} \frac{\partial^2}{\partial \gamma_\lambda^2} + \frac{1}{R_\lambda^2} \left(-J^2 - 2iJ \frac{\partial}{\partial \gamma_\lambda} + \frac{\partial^2}{\partial \gamma_\lambda^2} \right) \right] + V^\lambda - E \right\} \psi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = 0. \quad (2.14)$$

This equation is solved numerically by the method described in Secs. III and IV.

III. INTEGRATION OF THE SCHRÖDINGER EQUATION

A. The partitioning of configuration space into arrangement channel regions

We now wish to expand $\psi_J^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ in terms of sets of two-variable internal state basis functions in order to reduce the partial differential equation (2.14) to a system of coupled ordinary differential equations. Our choice for the internal state basis functions and the corresponding variables will be different in different regions of the three-dimensional internal configuration space $r_\lambda, R_\lambda, \gamma_\lambda$ and will be largely determined by the local shape of the potential energy function $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$. This is done in order to represent solutions of the full Schrödinger equation in an efficient manner in all regions of configuration space so as to reduce computation time as much as possible. A useful conceptualization of the nature of the problem can be gained by noting the appearance of the potential energy function $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$. This function is most conveniently displayed with the aid of a mapping procedure previously developed for this purpose.³⁰ In this mapping we consider a space $OX_\lambda Y_\lambda Z_\lambda$ in which a point P has spherical polar coordinates $\xi, \omega_\lambda, \gamma_\lambda$, where the radial variable ξ is defined by

$$\xi = (r_\lambda^2 + R_\lambda^2)^{1/2} \quad (3.1a)$$

and is independent of λ as shown in Eq. (A6) of Appendix A, and the polar angle ω_λ is defined by

$$\omega_\lambda = 2 \tan^{-1}(r_\lambda/R_\lambda), \quad 0 \leq \omega_\lambda \leq \pi. \quad (3.1b)$$

The azimuthal angle γ_λ has been defined after Eq. (2.1). Using the example of the $H+H_2$ reaction, the resulting contour plot of the Porter-Karplus³¹ potential for six different values of γ_λ is depicted in Fig. 2. This representation has the advantage of treating all three arrangement channels equivalently in that a change from coordinates λ to coordinates ν produces a clockwise rotation without distortion of Fig. 2 around the OY_λ axis by an angle of 120° .³⁰ We see from the figure that the accessible areas of configuration space are in the form of three tubelike regions whose mutual intersection defines the three-particle interaction region. For less symmetric potentials Fig. 2 would be less symmetric, but the considerations below have general validity.

Our approach for solving the Schrödinger equation consists of dividing the configuration space depicted in Fig. 2 into three subspaces called *arrangement channel regions* and labeled by the indices λ, ν, κ . Each of these three arrangement channel regions includes one

of the three tubes corresponding to a separated atom plus diatom, along with that part of the interaction region which retains the "general appearance" of that particular tube. For the $H+H_2$ system, a very natural separation of the three arrangement channel regions is obtained by the use of the three half-planes $\pi_{\nu\lambda}, \pi_{\kappa\nu}$, and $\pi_{\lambda\kappa}$ whose common edge is the OY_λ axis and which intersect the $OX_\lambda Z_\lambda$ plane in the symmetrical positions depicted in Fig. 2(a). A general definition of these three half-planes which is also applicable to reactions other than $H+H_2$ is

$$\pi_{\nu\lambda}: r_\lambda = r_\nu \quad 0 \leq \gamma_\lambda \leq \pi/2 \text{ and } 3\pi/2 \leq \gamma_\lambda < 2\pi, \quad (3.2a)$$

$$\pi_{\kappa\nu}: r_\nu = r_\kappa \quad 0 \leq \gamma_\nu \leq \pi/2 \text{ and } 3\pi/2 \leq \gamma_\nu < 2\pi, \quad (3.2b)$$

$$\pi_{\lambda\kappa}: r_\kappa = r_\lambda \quad 0 \leq \gamma_\kappa \leq \pi/2 \text{ and } 3\pi/2 \leq \gamma_\kappa < 2\pi. \quad (3.2c)$$

A proof that these equations do indeed define half-planes whose edge is the OY_λ axis, as graphically indicated in Fig. 2(a), is given in Appendix A along with the equations describing the λ to ν coordinate transformation. For some reactions, the half-planes defined above may be inadequate as they may not separate the three arrangement channel regions into physically intuitive ones as determined by the shape of the potential functions. In these cases, alternative surfaces may be chosen and treated by a straightforward extension of the theory presented in this paper. For the reactions $H+H_2$, $D+H_2$, $H+D_2$, etc., the half-planes of Eqs. (3.1) are quite satisfactory, so we shall proceed to formulate our theory using the arrangement channel regions into which they divide internal configuration space.

With the arrangement channel regions thus defined, we organize the work involved in solving Eq. (2.14) into two steps. First, within each of the three arrangement channel regions, we integrate the Schrödinger equation using rotational coordinates and basis functions appropriate to the asymptotic part of that arrangement channel but changing vibrational coordinates and basis functions in a way which transforms "smoothly" from one arrangement channel to another. Then, we match the resulting three sets of solutions to one another on the three half-planes $\pi_{\nu\lambda}, \pi_{\kappa\nu}, \pi_{\lambda\kappa}$ described above (and hereafter called the *matching surfaces*). Since the vibrational coordinates are designed to transform smoothly from one arrangement channel to the others, it is primarily the rotational parts of the wavefunctions which must be considered in the matching procedure. Our rotational expansion is similar to that of Saxon and Light,¹⁴ but not to that of Wyatt and co-workers,¹⁷ who allow both their vibrational and rotational coordinates to transform smoothly in going from one arrangement channel to the next.

In the remainder of this section, we will detail the method used for integrating the Schrödinger equation in each of the arrangement channel regions. The crucial smooth matching procedure is outlined in Sec. IV.

B. The rotationally coupled Schrödinger equations

We now consider the solution of Eq. (2.14) in each of the three arrangement channel regions $\lambda = \alpha, \beta, \gamma$.

The body-fixed rotational angular momentum operator

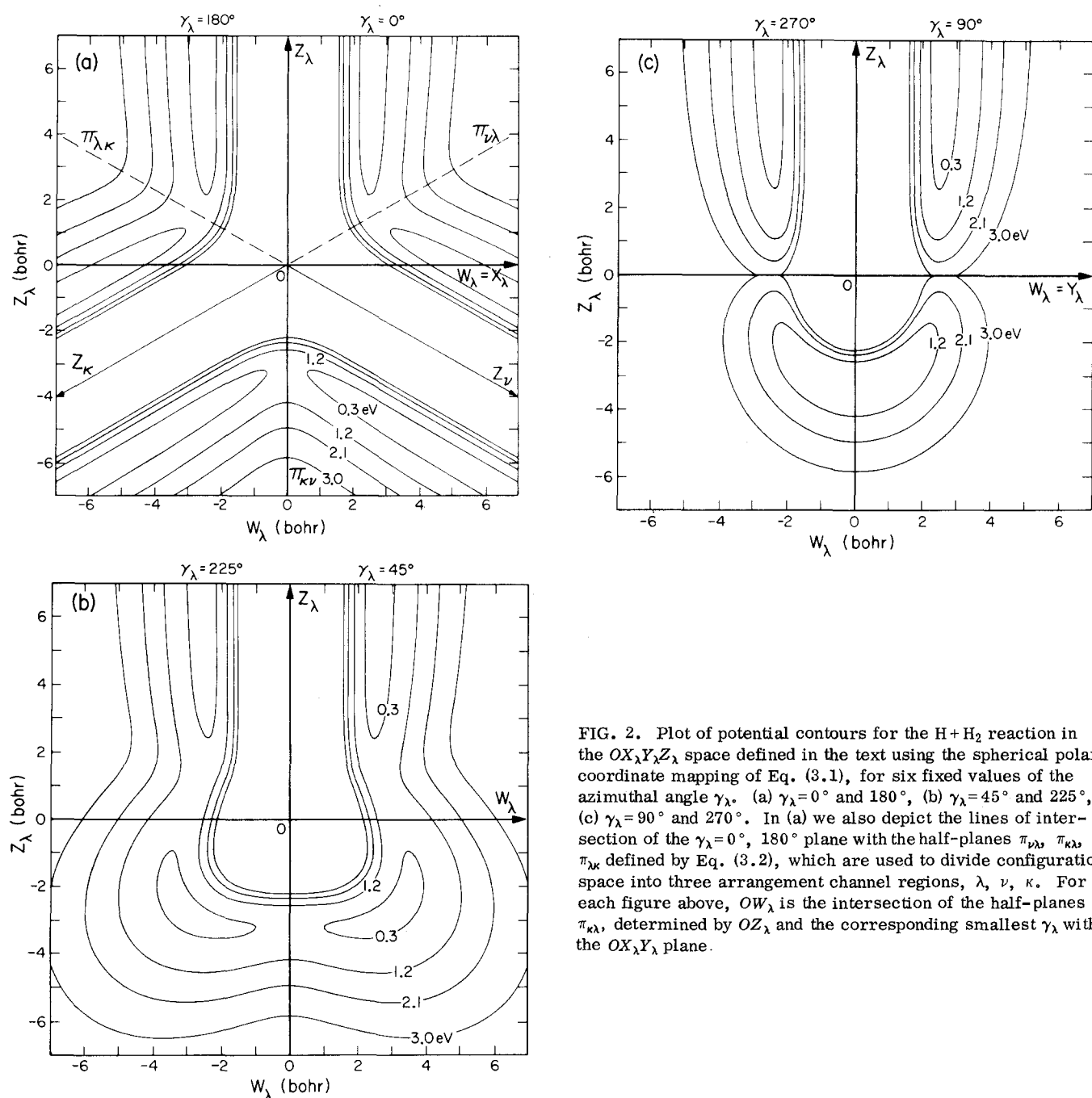


FIG. 2. Plot of potential contours for the $\text{H} + \text{H}_2$ reaction in the $\text{OX}_\lambda\text{Y}_\lambda\text{Z}_\lambda$ space defined in the text using the spherical polar coordinate mapping of Eq. (3.1), for six fixed values of the azimuthal angle γ_λ . (a) $\gamma_\lambda = 0^\circ$ and 180° , (b) $\gamma_\lambda = 45^\circ$ and 225° , (c) $\gamma_\lambda = 90^\circ$ and 270° . In (a) we also depict the lines of intersection of the $\gamma_\lambda = 0^\circ, 180^\circ$ plane with the half-planes $\pi_{\nu\lambda}$, $\pi_{\kappa\lambda}$, $\pi_{\kappa\nu}$ defined by Eq. (3.2), which are used to divide configuration space into three arrangement channel regions, λ , ν , κ . For each figure above, OW_λ is the intersection of the half-planes $\pi_{\nu\lambda}$, $\pi_{\kappa\lambda}$, determined by OZ_λ and the corresponding smallest γ_λ with the $\text{OX}_\lambda\text{Y}_\lambda$ plane.

j_λ associated with \mathbf{r}_λ is defined as

$$j_\lambda = \frac{\hbar}{i} \left(\frac{\partial}{\partial \gamma_\lambda} \right)_{\theta_\lambda, R_\lambda, r_\lambda} \hat{\mathbf{z}}, \quad (3.3)$$

and its eigenfunctions are

$$\varphi_{j_\lambda}(\gamma_\lambda) = (2\pi)^{-1/2} \exp(ij_\lambda\gamma_\lambda) \quad j_\lambda = 0, \pm 1, \pm 2, \dots \quad (3.4)$$

The expansion of ψ_j^λ , defined by Eq. (2.13), in terms of these eigenfunctions is

$$\psi_j^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = \sum_{j_\lambda} \varphi_{j_\lambda}(\gamma_\lambda) F_{jj_\lambda}^\lambda(r_\lambda, R_\lambda). \quad (3.5)$$

Substituting this into Eq. (2.14), taking the scalar product of both sides by $\varphi_{j'_\lambda}$, and interchanging the primed and unprimed quantum numbers, we obtain the following set of coupled partial differential equations in the two

scaled distances r_λ, R_λ :

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r_\lambda^2} + \frac{\partial^2}{\partial R_\lambda^2} - \frac{j_\lambda^2 - \frac{1}{4}}{r_\lambda^2} - \frac{(J - j_\lambda)^2 - \frac{1}{4}}{R_\lambda^2} \right) F_{jj_\lambda}^\lambda(r_\lambda, R_\lambda) \\ & + \sum_{j'_\lambda} V_{jj'_\lambda}^\lambda(r_\lambda, R_\lambda) F_{jj'_\lambda}^\lambda(r_\lambda, R_\lambda) \\ & = E F_{jj_\lambda}^\lambda(r_\lambda, R_\lambda) \quad J, j_\lambda = 0, \pm 1, \pm 2, \dots, \end{aligned} \quad (3.6)$$

where

$$\begin{aligned} V_{jj'_\lambda}^\lambda(r_\lambda, R_\lambda) &= \langle j_\lambda | V^\lambda | j'_\lambda \rangle \\ &= \int_0^{2\pi} \varphi_{j'_\lambda}^*(\gamma_\lambda) V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) \varphi_{j_\lambda}(\gamma_\lambda) d\gamma_\lambda. \end{aligned} \quad (3.7)$$

Since $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = V^\lambda(r_\lambda, R_\lambda, 2\pi - \gamma_\lambda)$, we can expand the potential in terms of a cosine Fourier series

$$V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = \sum_{k=0}^{\infty} V_k^\lambda(r_\lambda, R_\lambda) \cos(k\gamma_\lambda), \quad (3.8a)$$

where

$$V_k^\lambda(r_\lambda, R_\lambda) = \frac{2}{(1 + \delta_{k0})\pi} \int_0^\pi \cos(k\gamma_\lambda) V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) d\gamma_\lambda. \quad (3.8b)$$

Substituting Eq. (3.8) into (3.7) and integrating, we find that

$$\begin{aligned} V_{j_\lambda j'_\lambda}^\lambda(r_\lambda, R_\lambda) &= \frac{1}{2 - \delta_{|j_\lambda - j'_\lambda|, 0}} V_{|j_\lambda - j'_\lambda|}^\lambda(r_\lambda, R_\lambda) \\ &= \frac{1}{\pi} \int_0^\pi \cos(|j_\lambda - j'_\lambda| \gamma_\lambda) V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) d\gamma_\lambda. \end{aligned} \quad (3.9)$$

Equation (3.9) shows that $V_{j_\lambda j'_\lambda}^\lambda$ depends on j_λ and j'_λ only through $|j_\lambda - j'_\lambda|$. We can write Eq. (3.6) in a condensed matrix notation by regarding $\mathbf{F}_J^\lambda(r_\lambda, R_\lambda)$ as a column vector whose elements are the $F_{j_\lambda j'_\lambda}^\lambda(r_\lambda, R_\lambda)$. We get

$$T^\lambda \mathbf{F}_J^\lambda + \mathbf{V}_J^{\lambda e} \mathbf{F}_J^\lambda = E \mathbf{F}_J^\lambda, \quad (3.10)$$

where T^λ is the kinetic energy operator

$$T^\lambda = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\lambda^2} + \frac{\partial^2}{\partial r_\lambda^2} \right) \quad (3.11)$$

and $\mathbf{V}_J^{\lambda e}(r_\lambda, R_\lambda)$ is an effective potential energy matrix defined by

$$\mathbf{V}_J^{\lambda e}(r_\lambda, R_\lambda) = \mathbf{V}^\lambda(r_\lambda, R_\lambda) + \mathbf{V}_J^{\lambda c}(r_\lambda, R_\lambda). \quad (3.12)$$

\mathbf{V}^λ is the J -independent interaction potential matrix

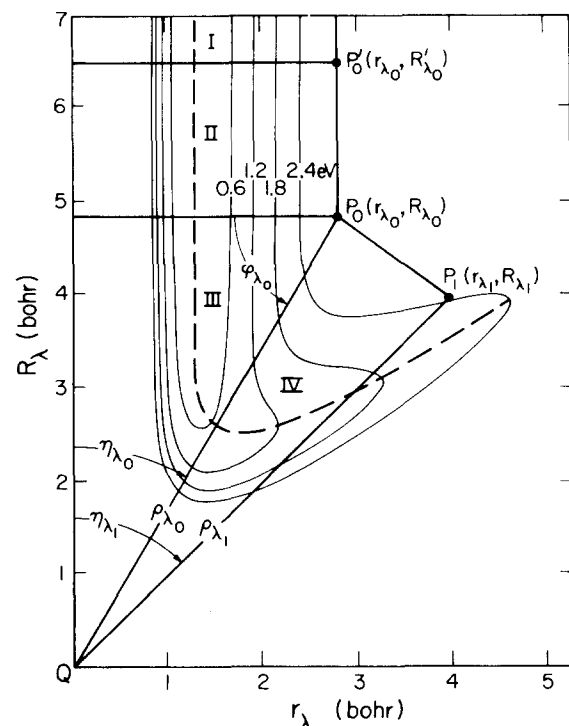


FIG. 3. Division of the R_λ, r_λ space into four regions, I, II, III, and IV. The contours are equipotentials of the matrix element $V_0^\lambda(r_\lambda, R_\lambda)$ [see Eq. (3.8)] in eV for the Porter-Karplus $\text{H} + \text{H}_2$ potential energy function. The dashed line L is the line of steepest ascents and descents for V_0^λ . The locations of the points P'_0 , P_0 , and P_1 are discussed in Sec. III.C of the text. Q is the origin of this space.

whose elements are the $V_{j_\lambda j'_\lambda}^\lambda$ defined by Eq. (3.9) while $\mathbf{V}_J^{\lambda c}$ is the diagonal centrifugal potential matrix defined by

$$[\mathbf{V}_J^{\lambda c}(r_\lambda, R_\lambda)]_{j_\lambda j'_\lambda} = \frac{\hbar^2}{2\mu} \left(\frac{j_\lambda^2 - \frac{1}{4}}{r_\lambda^2} + \frac{(J - j_\lambda)^2 - \frac{1}{4}}{R_\lambda^2} \right) \delta_{j_\lambda j'_\lambda}. \quad (3.13)$$

From Eqs. (3.6) and (3.9) we conclude that the $F_{j_\lambda j'_\lambda}^\lambda$ for different j_λ are coupled through the $V_k^\lambda(r_\lambda, R_\lambda)$ functions with $k > 0$, V_0^λ representing a noncoupling potential.

C. The division of r_λ, R_λ space into regions and the choice of variables in each region

We now consider the expansion of the function $F_{j_\lambda j'_\lambda}^\lambda(r_\lambda, R_\lambda)$ in terms of a set of single-variable functions which describe a vibrationlike motion. To pick this vibration variable and the corresponding vibrational basis set, it is convenient to examine the behavior of $V_0^\lambda(r_\lambda, R_\lambda)$ since, as one can conclude from the remark at the end of Sec. III.B, this function together with the centrifugal potential $(\hbar^2/2\mu)(j_\lambda^2 - \frac{1}{4})/r_\lambda^2$ determines the r_λ dependence of $F_{j_\lambda j'_\lambda}^\lambda$ in the absence of j_λ (i.e., rotational) coupling. For the $\text{H} + \text{H}_2$ reaction, equipotentials of $V_0^\lambda(r_\lambda, R_\lambda)$ are represented in Fig. 3, together with the corresponding line L of steepest ascents and descents. Cuts of V_0^λ normal to L look like diatomic internuclear potential energy functions, displaying a minimum on L , a dissociation plateau in the direction away from the coordinate axes, and a steep repulsive point in the opposite direction. These characteristics are analogous to those presented by collinear triatomic potential energy functions and suggest that we divide the r_λ, R_λ space in regions in a manner analogous to that employed for collinear reactions,^{5,10} using different coordinates and/or vibration basis functions in each region. The corresponding line L of steepest ascents and descents will be a distance along appropriately chosen lines transverse (but not necessarily orthogonal) to L . In each region, in addition to such vibration coordinates, there will be a "propagation" coordinate in terms of which Eq. (3.6), will be expressed as a system of coupled ordinary differential equations. For $\text{H} + \text{H}_2$ we indicate a convenient choice for these regions in Fig. 3. They are denoted as follows: I—the asymptotic region; II—the weak interaction region; III—the strong interaction region; and IV—the matching region. The boundary points P'_0 , P_0 , and P_1 in Fig. 3 are chosen as follows. The abscissa r_{λ_0} of P'_0 and P_0 is chosen so that these points lie in the classically forbidden plateau area where the wavefunction may be assumed to vanish. The ordinate R'_{λ_0} of P'_0 is picked large enough so that the potential $V_0^\lambda(r_\lambda, R_\lambda)$ is independent of R_λ for $R_\lambda \geq R'_{\lambda_0}$. R_{λ_0} is determined by setting η_{λ_0} of Fig. 3 equal to $\pi/2 - \alpha_{\nu\lambda}/2$, from which we get

$$R_{\lambda_0} = r_{\lambda_0} \tan(\alpha_{\nu\lambda}/2). \quad (3.14)$$

The reason for this choice is that in order to perform the matching of the different arrangement channel solutions, as described in Sec. III.A, we need the $F_{j_\lambda j'_\lambda}^\lambda$ defined by Eq. (3.5) for a range of values of η_λ . As justified after Eq. (3.18), the lower limit of this range is the η_{λ_0} just chosen. The same justification led to η_{λ_1}

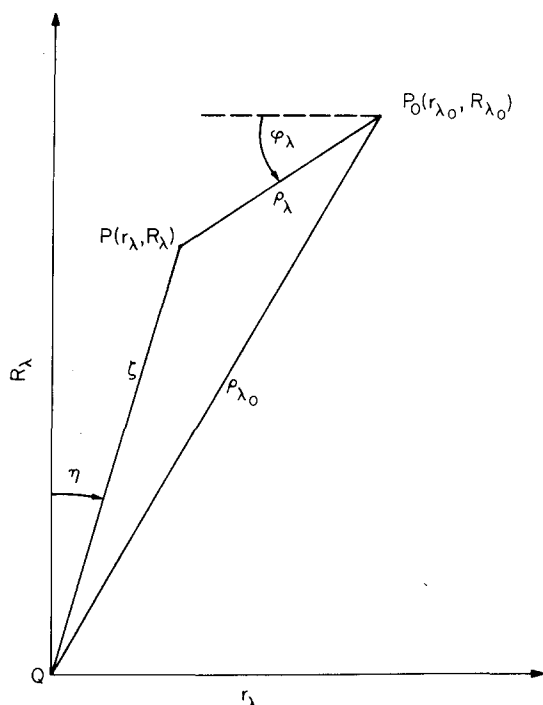


FIG. 4. The polar coordinates ρ_λ , φ_λ and ζ , η_λ and their interrelationships in R_λ , r_λ space.

$= \pi/4$, from which we get (see Fig. 3)

$$R_{\lambda_1} = r_{\lambda_1}. \quad (3.15)$$

This common value of R_{λ_1} and r_{λ_1} is chosen so that $P_1(r_{\lambda_1}, R_{\lambda_1})$ also lies in the plateau region.

The coordinate systems used in each of these four regions are as follows. In the asymptotic region (I) and in the weak interaction region (II), we use the Cartesian coordinates r_λ , R_λ as vibration and propagation coordinates, respectively. In the strong interaction region (III) we switch to the polar coordinates ρ_λ , φ_λ (as depicted in Fig. 4) with $P_0(r_{\lambda_0}, R_{\lambda_0})$ as origin and related to r_λ , R_λ by

$$r_\lambda = r_{\lambda_0} - \rho_\lambda \cos \varphi_\lambda, \quad (3.16a)$$

$$R_\lambda = R_{\lambda_0} - \rho_\lambda \sin \varphi_\lambda. \quad (3.16b)$$

ρ_λ is the vibration and φ_λ the propagation coordinate for this region. In the matching region (IV), we use another set of polar coordinates (ζ, η_λ) which have their origin at Q (Fig. 4) and which are related to r_λ , R_λ by

$$r_\lambda = \zeta \sin \eta_\lambda, \quad (3.17a)$$

$$R_\lambda = \zeta \cos \eta_\lambda. \quad (3.17b)$$

ζ (≥ 0) and η_λ (in range $0-\pi/2$) are, respectively, the vibration and propagation variables for Region IV. We note that the ζ defined here is identical to that given by Eq. (3.1a), while the angles ω_λ and η_λ are related, as can be seen from Eqs. (3.17) and (3.1b), by

$$\omega_\lambda = 2\eta_\lambda. \quad (3.18)$$

Once we know the $F_{JJ_\lambda}^\lambda$ functions for a fixed η_λ and variable ζ , Eq. (3.5) furnishes the wavefunction ψ_J^λ on a cone of constant ω_λ ($= 2\eta_\lambda$) in the $OX_\lambda Y_\lambda Z_\lambda$ coordinate system, as depicted in Fig. 5(a). We actually want to

determine this wavefunction on the matching surfaces $\pi_{\nu\lambda}$ and $\pi_{\lambda\kappa}$ rather than on the $\omega_\lambda = \text{constant}$ cones since it is on these surfaces that we will smoothly match the solutions obtained from the integration of the Schrödinger equation in the three arrangement channels $\lambda = \alpha, \beta, \gamma$. However, for a given ω_λ (within a certain range) we do have the wavefunctions on the lines of intersection of the constant ω_λ cone with the half-planes $\pi_{\nu\lambda}$ and $\pi_{\lambda\kappa}$ [see Fig. 5(a)]. The relation between ω_λ and γ_λ at the lines of intersection with $\pi_{\nu\lambda}$ is given by Eq. (A14) of Appendix A. As ω_λ is scanned from $\omega_{\lambda_0} = 2\eta_0$ to $\omega_{\lambda_1} = 2\eta_{\lambda_1}$ (Figs. 3 and 5), these intersection lines scan the entire $\pi_{\nu\lambda}$ matching half-plane and thus we can obtain the desired wavefunction ψ_J^λ on it from a knowledge of the $F_{JJ_\lambda}^\lambda(\zeta, \eta_\lambda)$ for η_λ in the range η_{λ_0} to η_{λ_1} . The angles ω_{λ_0} and ω_{λ_1} correspond to the intersection of $\pi_{\nu\lambda}$ with the $\gamma_\lambda = 0$ and $\gamma_\lambda = \pi/2$ half-plane, respectively (in $OX_\lambda Y_\lambda Z_\lambda$ internal configuration space). From Eq. (A14) we find that $\omega_{\lambda_0} = \pi - \alpha_{\nu\lambda}$ and $\omega_{\lambda_1} = \pi/2$. These values determine the values of η_{λ_0} and η_{λ_1} of Fig. 3 through Eq.

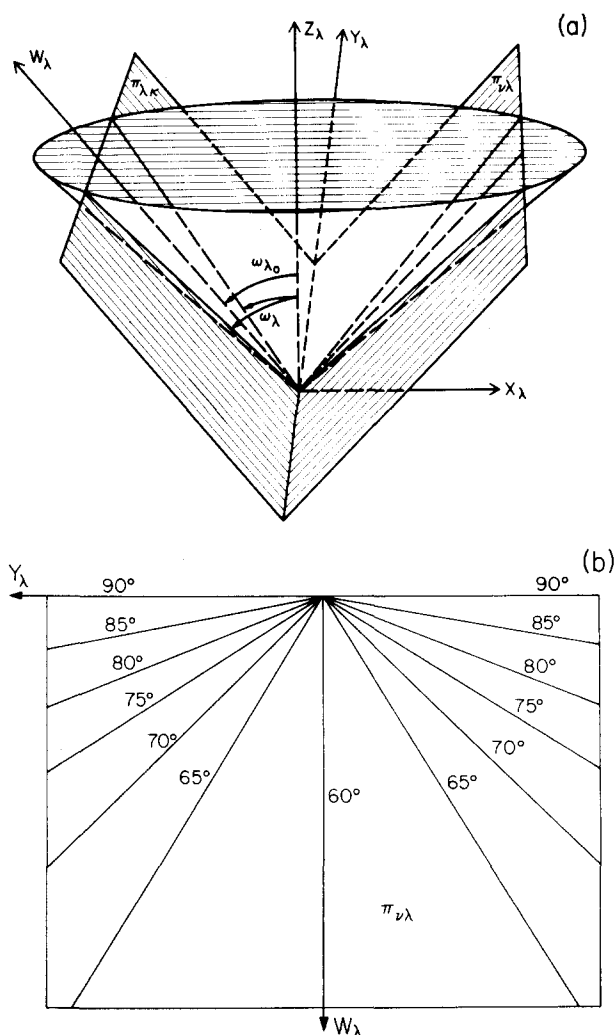


FIG. 5. (a) Plot of the matching half-planes $\pi_{\nu\lambda}$ and $\pi_{\lambda\kappa}$, and their intersection with a cone of constant ω_λ ($\omega_{\lambda_0} \leq \omega_\lambda \leq \omega_{\lambda_1}$) showing the straight lines of intersection which occur at two angles $\gamma_\lambda(\omega_\lambda)$ for which $\cot \omega_\lambda = -\cot \alpha_{\nu\lambda} \cos \gamma_\lambda$, and two more for which $\cot \omega_\lambda = \cot \alpha_{\lambda\kappa} \cos \gamma_\lambda$. (b) Lines of intersection of $\pi_{\nu\lambda}$ with constant ω_λ cones at intervals of $\Delta \omega_\lambda = 5^\circ$ for $H + H_2$, where $\omega_{\lambda_0} = 60^\circ$ and $\omega_{\lambda_1} = 90^\circ$.

(3.18), and consequently the positions of P_0 and P_1 . Indeed, by using Eqs. (3.17) and (3.18) together with the values of ω_{λ_0} and ω_{λ_1} given above, we obtain the equations (3.14) and (3.15) that were previously used in locating P_0 and P_1 .³² One additional complication in this procedure arises when $m_\nu \neq m_\kappa$ (for the integration in arrangement channel λ). In that case, the angles $\alpha_{\nu\lambda}$ and $\alpha_{\kappa\lambda}$ are different [see Eq. (A3)] so that the value of ω_{λ_0} for $\pi_{\nu\lambda}$ (i.e., $\omega_{\lambda_0} = \pi - \alpha_{\nu\lambda}$) is different from ω'_{λ_0} for $\pi_{\kappa\lambda}$ ($\omega'_{\lambda_0} = \pi - \alpha_{\kappa\lambda}$). In order to obtain the wavefunction on both of the matching surfaces $\pi_{\nu\lambda}$ and $\pi_{\kappa\lambda}$, we modify our definition of ω_{λ_0} to

$$\omega_{\lambda_0} = \min(\pi - \alpha_{\nu\lambda}, \pi - \alpha_{\kappa\lambda}). \quad (3.19)$$

ω_{λ_1} , on the other hand, is mass independent and always equal to $\pi/2$ for the choice of matching surfaces given by Eq. (3.2).

Having defined the four regions of each r_λ, R_λ space ($\lambda = \alpha, \beta, \gamma$) and their associated vibration-propagation coordinate systems, we are ready to introduce a vibrational expansion into the Schrödinger equations Eq. (3.6) [or their matrix counterpart Eq. (3.10)], thus obtaining the actual ordinary coupled differential equations to be integrated. We shall do this for each region separately, starting with the asymptotic region.

D. The coupled Schrödinger equations in the propagation variable

1. The asymptotic region

As mentioned above, the vibration and propagation variables for this region are r_λ and R_λ , respectively. The function $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ becomes the isolated diatomic potential $v^\lambda(r_\lambda)$ for $R_\lambda \geq R'_{\lambda_0}$, and the potential matrix \mathbf{V}^λ appearing in the right hand side of Eq. (3.12) becomes diagonal:

$$\mathbf{V}^\lambda(r_\lambda, R_\lambda \geq R_{\lambda_0}) = v^\lambda(r_\lambda) \mathbf{I}, \quad (3.20)$$

where \mathbf{I} is the identity matrix. This leads to a total decoupling of Eqs. (3.6) and (3.10). For a given J and j_λ , we obtain

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r_\lambda^2} + \frac{\partial^2}{\partial R_\lambda^2} - \frac{(j_\lambda^2 - \frac{1}{4})}{r_\lambda^2} + \frac{(J - j_\lambda)^2 - \frac{1}{4}}{R_\lambda^2} \right) + v^\lambda \right] F_{Jj_\lambda}^{\lambda(a)} = E F_{Jj_\lambda}^{\lambda(a)}, \quad (3.21)$$

where the superscript (a) refers to the asymptotic region. This equation may be solved by separation of variables. The solution can be expanded as

$$F_{Jj_\lambda}^{\lambda(a)}(r_\lambda, R_\lambda) = \sum_{v_\lambda} g_{Jv_\lambda j_\lambda}^{\lambda(a)}(R_\lambda) \phi_{v_\lambda j_\lambda}^{\lambda(a)}(r_\lambda), \quad (3.22)$$

where $\phi_{v_\lambda j_\lambda}^{\lambda(a)}$ is a vibrational eigenfunction with vibrational energy $\epsilon_{v_\lambda j_\lambda}^{\lambda(a)}$ satisfying the equation

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr_\lambda^2} + v^\lambda(r_\lambda) + \frac{j_\lambda^2 - \frac{1}{4}}{r_\lambda^2} \right) \phi_{v_\lambda j_\lambda}^{\lambda(a)} = \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} \phi_{v_\lambda j_\lambda}^{\lambda(a)} \quad (3.23)$$

with boundary conditions $\phi_{v_\lambda j_\lambda}^{\lambda(a)}(0) = \phi_{v_\lambda j_\lambda}^{\lambda(a)}(r_{\lambda_0}) = 0$. $g_{Jv_\lambda j_\lambda}^{\lambda(a)}(R_\lambda)$ describes the translational motion associated with the propagation variable, R_λ , and satisfies the equation

$$\left(\frac{d^2}{dR_\lambda^2} - \frac{(J - j_\lambda)^2 - \frac{1}{4}}{R_\lambda^2} + \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} \right) g_{Jv_\lambda j_\lambda}^{\lambda(a)} = 0, \quad (3.24)$$

where

$$k_{v_\lambda j_\lambda}^{\lambda(a)2} = \frac{2\mu}{\hbar^2} (E - \epsilon_{v_\lambda j_\lambda}^{\lambda(a)}) \quad (3.25)$$

is the square of the relative motion wave number when the diatom is in the vibration-rotation state labeled by the quantum numbers v_λ, j_λ . Equation (3.24) is closely related to the Bessel equation, and its general solution can be written as

$$g_{Jv_\lambda j_\lambda}^{\lambda(a)}(R_\lambda) = \left(|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda \right)^{1/2} \begin{cases} a_{Jv_\lambda j_\lambda}^{\lambda(a)} J_{J-j_\lambda}(k_{v_\lambda j_\lambda}^{\lambda(a)} R_\lambda) + c_{Jv_\lambda j_\lambda}^{\lambda(a)} Y_{J-j_\lambda}(k_{v_\lambda j_\lambda}^{\lambda(a)} R_\lambda) & \text{for } \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} < E \text{ (open channels)} \\ a_{Jv_\lambda j_\lambda}^{\lambda(a)} I_{J-j_\lambda}(|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda) + c_{Jv_\lambda j_\lambda}^{\lambda(a)} K_{J-j_\lambda}(|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda) & \text{for } \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} > E \text{ (closed channels)}. \end{cases} \quad (3.26)$$

The functions J_l and Y_l are, respectively, the regular and irregular ordinary Bessel functions³³ of order l and have the asymptotic behavior

$$x^{1/2} J_l(x) \underset{x \rightarrow \infty}{\sim} (2/\pi)^{1/2} \cos(x - l\pi/2 - \pi/4), \quad (3.27a)$$

$$x^{1/2} Y_l(x) \underset{x \rightarrow \infty}{\sim} (2/\pi)^{1/2} \sin(x - l\pi/2 - \pi/4), \quad (3.27b)$$

whereas I_l and K_l are the modified Bessel functions³³ and have the asymptotic behavior

$$x^{1/2} I_l(x) \underset{x \rightarrow \infty}{\sim} (2\pi)^{-1/2} \exp(x), \quad (3.28a)$$

$$x^{1/2} K_l(x) \underset{x \rightarrow \infty}{\sim} (\pi/2)^{1/2} \exp(-x). \quad (3.28b)$$

In Sec. V we will consider scattering asymptotic conditions which will determine the constants $a_{Jv_\lambda j_\lambda}^{\lambda(a)}$ and $c_{Jv_\lambda j_\lambda}^{\lambda(a)}$.

Let us rewrite Eqs. (3.24) and (3.26) in matrix notation, which will appreciably simplify the equations in the rest of the paper. Let $\mathbf{g}_{Jj_\lambda}^{\lambda(a)}(R_\lambda)$ be the column vec-

tor whose elements, labeled by the $v_\lambda j_\lambda$ index pair, are given by Eq. (3.26). When replaced into Eqs. (3.22), (3.5), and (2.13), it furnishes a single $\chi_J^\lambda(R_\lambda, r_\lambda, \gamma_\lambda)$, corresponding to a single $\mathbf{a}_J^\lambda, \mathbf{c}_J^\lambda$ column vector pair, the elements of which are the $a_{Jv_\lambda j_\lambda}^{\lambda(a)}$ and $c_{Jv_\lambda j_\lambda}^{\lambda(a)}$ of Eq. (3.26). In order to satisfy Condition (c) of Sec. II.A, we will need a complete set of linearly independent solutions of the Schrödinger equation. The number of solutions in such a set is twice the number of $v_\lambda j_\lambda$ channels included in the expansions of Eqs. (3.22) and (3.5), which should be infinite but for practical reasons are truncated at a finite number N . (The errors introduced by this truncation will be discussed subsequently.²⁰) We can assemble the corresponding $\mathbf{g}_{Jj_\lambda}^{\lambda(a)}$ vectors to form two square matrices of dimension $N \times N$ which we shall label $\mathbf{g}_{Jj_\lambda}^{\lambda(a)+}(R_\lambda)$ and $\mathbf{g}_{Jj_\lambda}^{\lambda(a)-}(R_\lambda)$. In each of these two matrices, the rows will be labeled by (v_λ, j_λ) pairs and the columns by (v'_λ, j'_λ) pairs. In the course of our integration, we will obtain the solutions labeled $(+)$ by a

propagation from Region I to IV and those labeled $(-)$ by a propagation in the opposite direction. If we similarly form the matrices \mathbf{a}_J^\pm and \mathbf{c}_J^\pm from the corresponding \mathbf{a}_J^\pm and \mathbf{c}_J^\pm vectors, we can rewrite Eqs. (3.24) and (3.26) as

$$\frac{d^2 \mathbf{g}_J^{\lambda(a)\pm}}{dR_\lambda^2} = \mathbf{U}_J^{\lambda(a)}(R_\lambda) \mathbf{g}_J^{\lambda(a)\pm} \quad (3.29)$$

and

$$[\mathbf{J}_J^\lambda]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = (|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda)^{1/2} \delta_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} \begin{cases} Y_{J-j_\lambda}(k_{v_\lambda j_\lambda}^{\lambda(a)} R_\lambda) & \text{for } \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} < E \text{ (open channels)} \\ I_{J-j_\lambda}(|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda) & \text{for } \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} > E \text{ (closed channels)} \end{cases} \quad (3.34)$$

$$[\mathbf{Y}_J^\lambda]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = (|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda)^{1/2} \delta_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} \begin{cases} Y_{J-j_\lambda}(k_{v_\lambda j_\lambda}^{\lambda(a)} R_\lambda) & \text{for } \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} < E \text{ (open channels)} \\ K_{J-j_\lambda}(|k_{v_\lambda j_\lambda}^{\lambda(a)}| R_\lambda) & \text{for } \epsilon_{v_\lambda j_\lambda}^{\lambda(a)} > E \text{ (closed channels)} \end{cases} \quad (3.35)$$

In Eqs. (3.32) through (3.35) the subscripts in a matrix element represent its row label and the superscripts its column label. Equations analogous to Eq. (3.29) will be developed for each of the other three subregions. Equation (3.30) and similar equations will be used in the reactance matrix analysis (Sec. V).

2. The weak interaction region

In this region, we retain the vibration-propagation variables r_λ, R_λ . However, since $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ and $\mathbf{V}^\lambda(r_\lambda, R_\lambda)$ do vary with R_λ , the asymptotic vibrational eigenfunctions $\phi_{v_\lambda j_\lambda}^{\lambda(a)}$ are not necessarily the best basis for expanding the $F_{J,j_\lambda}^\lambda(r_\lambda, R_\lambda)$. To optimize a choice of basis functions, we divide Region II into n_{II} subregions Π_i ($i=1, 2, \dots, n_{II}$) by constant R_λ lines having $R_\lambda = (R'_{\lambda 0}, R'_{\lambda 1}, \dots, R'_{\lambda n_{II}} = R_{\lambda 0})$. The range of R_λ for the i th subregion is $R'_{\lambda i-1} \leq R_\lambda \leq R'_{\lambda i}$. Let $R_{\lambda i}^0$ be a selected value of R_λ in this range, such as its midpoint. We choose as a basis set for expansion in this subregion the functions $\phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0)$ which satisfy the eigenvalue equation

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr_\lambda^2} + V_{\text{ref}}^\lambda(r_\lambda; R_{\lambda i}^0) + \frac{(j_\lambda^2 - \frac{1}{4})\hbar^2}{2\mu r_\lambda^2} \right) \phi_{v_\lambda j_\lambda}^{\lambda(w)} = \epsilon_{v_\lambda j_\lambda}^{\lambda(w)}(R_{\lambda i}^0) \phi_{v_\lambda j_\lambda}^{\lambda(w)} \quad (3.36)$$

with boundary conditions $\phi_{v_\lambda j_\lambda}^{\lambda(w)}(0; R_{\lambda i}^0) = \phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_{\lambda 0}; R_{\lambda i}^0) = 0$. The superscript (w) refers to the weak interaction region. $V_{\text{ref}}^\lambda(r_\lambda; R_{\lambda i}^0)$ is the value of a reference potential $V_{\text{ref}}^\lambda(r_\lambda, R_\lambda)$ at $R_\lambda = R_{\lambda i}^0$. It is, in principle, arbitrary, but in practice must be chosen so that the vibrational basis functions $\phi_{v_\lambda j_\lambda}^{\lambda(w)}$ serve as an efficient representation of the r_λ dependence of the functions $F_{J,j_\lambda}^\lambda(r_\lambda, R_\lambda)$. Examples of possible reference potentials are (a) the first coefficient in the Fourier expansion [Eq. (3.8)] $V_0^\lambda(r_\lambda, R_\lambda)$, and (b) the exact potential $V^\lambda(R_\lambda, r_\lambda, \gamma_\lambda)$ for a fixed γ_λ . One important test of vibrational convergence in our method is the invariance of the final re-

$$\mathbf{g}_J^{\lambda(a)\pm}(R_\lambda) = \mathbf{J}_J^\lambda(R_\lambda) \mathbf{a}_J^{\lambda\pm} + \mathbf{Y}_J^\lambda(R_\lambda) \mathbf{c}_J^{\lambda\pm}, \quad (3.30)$$

where

$$\mathbf{U}_J^{\lambda(a)} = -\mathbf{K}^{\lambda(a)2} + \mathbf{U}_J^{c\lambda(a)}, \quad (3.31)$$

$$[\mathbf{K}^{\lambda(a)2}]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \delta_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} k_{v_\lambda j_\lambda}^{\lambda(a)2}, \quad (3.32)$$

$$[\mathbf{U}_J^{c\lambda(a)}]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \delta_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} \frac{(J-j_\lambda)^2 - \frac{1}{4}}{R_\lambda^2}, \quad (3.33)$$

sults to the choice of V_{ref}^λ . Equation (3.35) is the radial Schrödinger equation of a pseudomolecule whose interatomic potential is $V_{\text{ref}}^\lambda(r_\lambda; R_{\lambda i}^0)$, characteristic of Subregion Π_i , rather than $v^\lambda(r_\lambda)$, which characterizes the asymptotic region. [Its centrifugal potential is, however, not the normal $j_\lambda(j_\lambda+1)\hbar^2/2\mu r_\lambda^2$ one.] The $\phi_{v_\lambda j_\lambda}^{\lambda(w)}$ and $\epsilon_{v_\lambda j_\lambda}^{\lambda(w)}$ are obtained by numerically solving Eq. (3.36),³⁴ subject to the boundary conditions just mentioned.

We now expand $F_{J,j_\lambda}^\lambda(r_\lambda, R_\lambda)$ in terms of the above vibrational basis functions:

$$F_{J,j_\lambda}^{\lambda(w)\pm}(r_\lambda, R_\lambda) = \sum_{v_\lambda} g_{J,j_\lambda}^{\lambda(w)\pm}(R_\lambda; R_{\lambda i}^0) \phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0). \quad (3.37)$$

Substituting this into Eq. (3.6), multiplying by $\phi_{v'_\lambda j'_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0)$ and integrating over r_λ , then interchanging v_λ and v'_λ and expressing the resulting coupled equations in the matrix form of the previous section, we get

$$\frac{d^2 \mathbf{g}_J^{\lambda(w)\pm}}{dR_\lambda^2} = \mathbf{U}_J^{\lambda(w)}(R_\lambda; R_{\lambda i}^0) \mathbf{g}_J^{\lambda(w)\pm}, \quad (3.38)$$

where

$$\mathbf{U}_J^{\lambda(w)} = -\mathbf{K}^{\lambda(w)2} + \mathbf{U}_J^{c\lambda(w)} + \mathbf{U}_J^{p\lambda(w)}. \quad (3.39)$$

The diagonal matrices $\mathbf{K}^{\lambda(w)2}$ and $\mathbf{U}_J^{c\lambda(w)}$ are defined by Eqs. (3.32) and (3.33), respectively, with the superscript (a) replaced by (w) , while the J -independent coupling "potential" matrix $\mathbf{U}_J^{p\lambda(w)}(R_\lambda; R_{\lambda i}^0)$ (whose physical dimension is that of the square of a wave number) is given by

$$\begin{aligned} [\mathbf{U}_J^{p\lambda(w)}(R_\lambda; R_{\lambda i}^0)]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} &= \frac{2\mu}{\hbar^2} \langle \phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0) | V_{J,j_\lambda}^\lambda(r_\lambda, R_\lambda) - V_{\text{ref}}^\lambda(r_\lambda; R_{\lambda i}^0) | \phi_{v'_\lambda j'_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0) \rangle \\ &= \frac{2\mu}{\hbar^2} \langle \phi_{v_\lambda j_\lambda}^\lambda(r_\lambda) \phi_{v'_\lambda j'_\lambda}^\lambda(r_\lambda; R_{\lambda i}^0) | V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - V_{\text{ref}}^\lambda(r_\lambda; R_{\lambda i}^0) | \phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0) \phi_{v'_\lambda j'_\lambda}^\lambda(r_\lambda) \rangle \\ &= \frac{2\mu}{\hbar^2} \langle v_\lambda j_\lambda | V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - V_{\text{ref}}^\lambda(r_\lambda; R_{\lambda i}^0) | v'_\lambda j'_\lambda \rangle. \end{aligned} \quad (3.40)$$

As long as the anisotropy of the potential remains small and the reference potential provides an efficient vibrational basis set for expanding the functions $F_{j,j_\lambda}^\lambda(r_\lambda; R_\lambda)$ within each subregion, the matrix $\mathbf{U}_j^{(\omega)}$ should be nearly diagonal, and Eqs. (3.38) are only weakly coupled. The number and size of the subregions into which Region II is divided depends on the steepness of the variation of the potential matrix $\langle v_{\lambda,j_\lambda} | V^\lambda | v_{\lambda,j'_\lambda} \rangle$ with R_λ . This number is generally small (i.e., less than 3).

As we propagate the solutions of Eq. (3.38) through Region II towards Regions I or III, the wavefunctions $\chi_{j,j_\lambda}^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ must remain continuous and smooth during the change of basis functions that occurs at the boundaries of neighboring subregions. This requirement leads to the following relations between the functions $g_{j,j_\lambda}^\lambda(R_\lambda; R_{\lambda i}^0)$ and $g_{j,j_\lambda}^\lambda(R_\lambda; R_{\lambda i+1}^0)$ and their derivatives at the boundary of Subregions II_i and II_{i+1}:

$$\mathbf{g}_{j,j_\lambda}^{\lambda(w)*}(R_{\lambda i}'; R_{\lambda i+1}^0) = \mathbf{S}_i^{\lambda(w)} \mathbf{g}_{j,j_\lambda}^{\lambda(w)*}(R_{\lambda i}'; R_{\lambda i}^0), \quad (3.41a)$$

$$\frac{d\mathbf{g}_{j,j_\lambda}^{\lambda(w)*}}{dR_\lambda}(R_{\lambda i}'; R_{\lambda i+1}^0) = \mathbf{S}_i^{\lambda(w)} \frac{d\mathbf{g}_{j,j_\lambda}^{\lambda(w)*}}{dR_\lambda}(R_{\lambda i}'; R_{\lambda i}^0), \quad (3.41b)$$

where the overlap matrix $\mathbf{S}_i^{\lambda(w)}$ is given by

$$[\mathbf{S}_i^{\lambda(w)}]_{v_{\lambda,j_\lambda}^0 v_{\lambda,j'_\lambda}^0} = \delta_{j_\lambda,j'_\lambda} \langle \phi_{v_{\lambda,j_\lambda}^0}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0) | \phi_{v_{\lambda,j'_\lambda}^0}^{\lambda(w)}(r_\lambda; R_{\lambda i}^0) \rangle. \quad (3.42)$$

An important criterion for the choice of the size of the subregions is that the $\mathbf{S}_i^{\lambda(w)}$ should be nearly orthogonal matrices. Lack of orthogonality implies lack of completeness of the basis sets $\phi_{v_{\lambda,j_\lambda}^0}^{\lambda(w)}$ and results in the loss of information about the wavefunction as a result of the transformation of Eqs. (3.41). The relations at the boundary separating Regions I and II are achieved by setting $i=0$ in Eqs. (3.41) and interpreting $R_{\lambda 0}^0$ to mean $R_{\lambda 0}'$ and $\phi_{v_{\lambda,j_\lambda}^0}^{\lambda(w)}(r_\lambda; R_{\lambda 0}^0)$ to mean $\phi_{v_{\lambda,j_\lambda}^0}^{\lambda(w)}(r_\lambda)$.

3. The strong interaction region

In this region we use the polar coordinates $\rho_\lambda, \varphi_\lambda$ regarding φ_λ as the propagation variable. If we transform Eq. (3.10) to these polar coordinates with the aid of Eq. (3.16), we obtain the vector equation

$$T^{\lambda(s)} \mathbf{F}_j^{(s)}(\rho_\lambda, \varphi_\lambda) + \mathbf{V}_j^{(s)} \mathbf{F}_j^{(s)} = E \mathbf{F}_j^{(s)}, \quad (3.43)$$

where the superscript (s) refers to "strong interaction region." $T^{\lambda(s)}$ is given by

$$T^{\lambda(s)} = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial \rho_\lambda^2} + \frac{1}{\rho_\lambda} \frac{\partial}{\partial \rho_\lambda} + \frac{1}{\rho_\lambda^2} \frac{\partial^2}{\partial \varphi_\lambda^2} \right), \quad (3.44)$$

and the matrix $\mathbf{V}_j^{(s)}(\rho_\lambda, \varphi_\lambda)$ is simply $\mathbf{V}_j^s(r_\lambda, R_\lambda)$ expressed in the coordinates $\rho_\lambda, \varphi_\lambda$.

For a typical reference potential V_{ref}^λ such as the $V_0^\lambda(r_\lambda, R_\lambda)$ defined by Eq. (3.8b) and plotted in Fig. 3 for $\text{H} + \text{H}_2$, the shape of the potential as a function of ρ_λ for a fixed $\varphi_\lambda (0 \leq \varphi_\lambda \leq \varphi_{\lambda 0})$ is very much like that for a diatomic molecule. The deep potential well character of these cuts at constant φ_λ permits one to use their bound state eigenfunctions to efficiently represent the ρ_λ dependence of the wavefunction in this region. Accordingly, we divide Region III into n_{III}^λ subregions III_i ($i=1, 2, \dots, n_{\text{III}}^\lambda$) by lines of constant

$$\varphi_\lambda(\varphi_\lambda = 0, \varphi_{\lambda 1}', \varphi_{\lambda 2}', \dots, \varphi_{\lambda n_{\text{III}}^\lambda}' = \varphi_{\lambda 0}).$$

For each such subregion, we choose a cut at a specific value $\varphi_{\lambda i}^0$ of φ_λ (where $\varphi_{\lambda i-1}^0 \leq \varphi_{\lambda i}^0 \leq \varphi_{\lambda i+1}^0$) to define our vibrational basis functions $\phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_{\lambda i}^0)$ and energy eigenvalues $\epsilon_{v_\lambda}^{\lambda(s)}(\varphi_{\lambda i}^0)$ as the solutions of the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho_\lambda^2} + V_{\text{ref}}^\lambda(\rho_\lambda; \varphi_{\lambda i}^0) \right) \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_{\lambda i}^0) = \epsilon_{v_\lambda}^{\lambda(s)}(\varphi_{\lambda i}^0) \phi_{v_\lambda}^{\lambda(s)}, \quad (3.45)$$

satisfying the boundary conditions $\phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda = 0) = \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda = \rho_{\lambda i}') = 0$, where $\rho_{\lambda i}'$ is the value of ρ_λ at the intersection of the line $\varphi_\lambda = \varphi_{\lambda i}^0$ with the R_λ axis (Fig. 3). The potential $V_{\text{ref}}^\lambda(\rho_\lambda, \varphi_\lambda)$ is one of the reference potentials $V_{\text{ref}}^\lambda(r_\lambda, R_\lambda)$ defined in Sec. III.D.2 expressed in $\rho_\lambda, \varphi_\lambda$ coordinates. Note that we have not included any j_λ -dependent centrifugal terms in the Hamiltonian of Eq. (3.45) (all of these terms being included in the "propagation part" of the Hamiltonian), and hence our eigenvalues and eigenfunctions depend only on the vibrational quantum number v_λ . This is done for computational convenience and does not seriously decrease the rate of convergence of our coupled-channel expansion.

We now expand the solutions $\mathbf{F}_j^{(s)}$ of Eq. (3.43) in terms of the pseudovibrational functions $\phi_{v_\lambda}^{\lambda(s)}$,

$$\mathbf{F}_{j,j_\lambda}^{\lambda(s)*}(\rho_\lambda, \varphi_\lambda) = \rho_\lambda^{-1/2} \sum_{v_\lambda} g_{j,j_\lambda}^{\lambda(s)*}(\varphi_\lambda; \varphi_{\lambda i}^0) \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_{\lambda i}^0). \quad (3.46)$$

The counterpart of Eq. (3.38) becomes

$$\frac{d^2 \mathbf{g}_{j,j_\lambda}^{\lambda(s)*}}{d\varphi_\lambda^2} = \bar{\mathbf{U}}_j^{\lambda(s)}(\varphi_\lambda; \varphi_{\lambda i}^0) \mathbf{g}_{j,j_\lambda}^{\lambda(s)*}, \quad (3.47)$$

where the effective "potential" matrix $\bar{\mathbf{U}}_j^{\lambda(s)}$ (whose elements are dimensionless) can be written as

$$\bar{\mathbf{U}}_j^{\lambda(s)} = \rho_{\lambda i}^2(\varphi_{\lambda i}^0) \mathbf{U}_j^{\lambda(s)}(\varphi_\lambda; \varphi_{\lambda i}^0), \quad (3.48)$$

in which

$$\mathbf{U}_j^{\lambda(s)} = -\mathbf{K}^{\lambda(s)2} + \mathbf{U}_j^{c\lambda(s)} + \mathbf{U}_j^{\lambda(s)}.$$

The matrix $\rho_{\lambda i}^2$ is given by

$$[\rho_{\lambda i}^2(\varphi_{\lambda i}^0)]_{v_{\lambda,j_\lambda}^0 v_{\lambda,j'_\lambda}^0} = \langle v_{\lambda,j_\lambda}^0 | \rho_{\lambda i}^2 | v_{\lambda,j'_\lambda}^0 \rangle \delta_{j_\lambda,j'_\lambda}. \quad (3.49)$$

The matrix $\mathbf{K}^{\lambda(s)2}$ and the "potential" coupling matrix $\mathbf{U}_j^{\lambda(s)}$ are quite similar to those in Eqs. (3.32) and (3.40) and are given by

$$[\mathbf{K}^{\lambda(s)2}(\varphi_{\lambda i}^0)]_{v_{\lambda,j_\lambda}^0 v_{\lambda,j'_\lambda}^0} = \delta_{v_{\lambda,j_\lambda}^0 v_{\lambda,j'_\lambda}^0} \frac{2\mu}{\hbar^2} [E - \epsilon_{v_\lambda}^{\lambda(s)}(\varphi_{\lambda i}^0)] \quad (3.50)$$

and

$$[\mathbf{U}_j^{\lambda(s)}(\varphi_\lambda; \varphi_{\lambda i}^0)]_{v_{\lambda,j_\lambda}^0 v_{\lambda,j'_\lambda}^0} = \frac{2\mu}{\hbar^2} \langle \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_{\lambda i}^0) | V_{j,j_\lambda}^\lambda(\rho_\lambda, \varphi_\lambda) - V_{\text{ref}}^\lambda(\rho_\lambda; \varphi_{\lambda i}^0) | \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_{\lambda i}^0) \rangle, \quad (3.51)$$

respectively, but the centrifugal potential matrix is now defined as

$$[\mathbf{U}_j^{c\lambda(s)}(\varphi_\lambda; \varphi_{\lambda i}^0)]_{v_{\lambda,j_\lambda}^0 v_{\lambda,j'_\lambda}^0} = \langle v_{\lambda,j_\lambda}^0 | \frac{j_\lambda^2 - \frac{1}{4}}{(r_{\lambda 0} - \rho_\lambda \cos \varphi_\lambda)^2} + \frac{(j - j_\lambda)^2 - \frac{1}{4}}{(R_{\lambda 0} - \rho_\lambda \sin \varphi_\lambda)^2} - \frac{1}{4\rho_\lambda^2} | v_{\lambda,j'_\lambda}^0 \rangle \delta_{j_\lambda,j'_\lambda}, \quad (3.52)$$

where the first term between vertical bars in Eq. (3.52)

arises from the rotation of the diatom, the second from rotation of the atom-diatom system, and the third is a pseudocentrifugal potential arising from the use of the ρ_λ , φ_λ coordinates and associated with the nonphysical swinging motion around the point P_0 of Fig. 3 as φ_λ is changed. The centrifugal coupling [Eq. (3.52)] is still diagonal in j_λ [as is its counterpart for the (a) and (w) regions] but no longer in v_λ . In addition to the usual potential coupling resulting from the off-diagonal terms of $\mathbf{U}_J^{(s)}$, we also have coupling arising from the nondiagonal ρ_λ^2 matrix which appears in Eq. (3.48) as a result of the swinging motion around P_0 . The neglect of this latter coupling could introduce serious errors since ρ_λ^2 has large off-diagonal elements. Such an approximation has nevertheless often been used,^{14,15} since it is one of the consequences of the one-vibrational-basis-function approximation. Note also that the effective potential matrix $\mathbf{U}_J^{(s)}$ is not symmetric, but is the product of two symmetric matrices as can be seen from Eq. (3.48). In Sec. III.E we discuss the Gordon method³⁵ used to integrate Eq. (3.47) and the modifications of it which are required when dealing with matrices of this type.

The smooth matching across the boundary separating any two neighboring subregions III_i and III_{i+1} is achieved through expressions analogous to Eqs. (3.41) in which the overlap matrix \mathbf{S}_i^λ is given by

$$[\mathbf{S}_i^\lambda(\varphi_\lambda^0)]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \delta_{j_\lambda j'_\lambda} \langle \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_\lambda^0) | \phi_{v'_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_\lambda^0) \rangle \quad (3.53)$$

and has elements which are independent of j_λ , j'_λ . Since the general characteristics of the ρ_λ dependence of the reference potential $V_{\text{ref}}^\lambda(\rho_\lambda, \varphi_\lambda)$ usually change quite rapidly as φ_λ is changed, the number of subregions in Region III required to keep \mathbf{S}_i^λ nearly orthogonal for a truncated vibrational basis set is generally large (on the order of 20–30).

The smooth matching of the wavefunction χ^λ across the boundary between Regions II and III is achieved by the relations

$$\mathbf{g}_J^{\lambda(s)*}(\varphi_\lambda = 0; \varphi_\lambda^0) = \rho_\lambda^{1/2} \mathbf{g}_J^{\lambda(w)*}(R_{\lambda 0}; R_{\lambda n_{\text{III}}}^0) \quad (3.54a)$$

and

$$\frac{d\mathbf{g}_J^{\lambda(s)*}}{d\varphi_\lambda}(\varphi_\lambda = 0; \varphi_\lambda^0) = -\rho_\lambda^{3/2} \frac{d\mathbf{g}_J^{\lambda(w)*}}{dR_\lambda}(R_{\lambda 0}; R_{\lambda n_{\text{III}}}^0), \quad (3.54b)$$

where

$$(\rho_\lambda^b)_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \langle \phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda; \varphi_\lambda^0) | \rho_\lambda^b | \phi_{v'_\lambda}^{\lambda(w)}(r_{\lambda 0} - \rho_\lambda; R_{\lambda n_{\text{III}}}^0) \rangle \delta_{j_\lambda j'_\lambda} \quad (3.55)$$

$$b = \frac{1}{2}, \frac{3}{2}.$$

4. The matching region

As described in Sec. III.C, the coordinates used in this region are the polar variables ζ , η_λ depicted in Fig. 4, with η_λ being the propagation variable. The Schrödinger equation in Region IV is very similar to that in Region III [see Eqs. (3.43)–(3.52)] with ρ_λ , φ_λ replaced by ζ , η_λ . From Eqs. (3.17) and (3.10) we obtain the counterpart of Eq. (3.43):

$$T^{\lambda(m)} \mathbf{F}_J^{\lambda(m)}(\zeta, \eta_\lambda) + \mathbf{V}_J^{\lambda(s)(m)}(\zeta, \eta_\lambda) \mathbf{F}_J^{\lambda(m)} = E \mathbf{F}_J^{\lambda(m)}, \quad (3.56)$$

where

$$T^{\lambda(m)} = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial \zeta^2} + \frac{1}{\zeta} \frac{\partial}{\partial \zeta} + \frac{1}{\zeta^2} \frac{\partial^2}{\partial \eta_\lambda^2} \right). \quad (3.57)$$

The superscript (m) denotes “matching region,” and $\mathbf{V}_J^{\lambda(s)(m)}(\zeta, \eta_\lambda)$ is obtained from $\mathbf{V}_J^{\lambda(s)}(r_\lambda, R_\lambda)$ by using Eq. (3.17). The division of Region IV into subregions is analogous to that for Regions II and III, and the vibrational basis functions $\phi_{v_\lambda}^{\lambda(m)}(\zeta; \eta_{\lambda i}^0)$ with eigenvalue $\epsilon_{v_\lambda}^{\lambda(m)}(\eta_{\lambda i}^0)$ satisfy the equation

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{d\zeta^2} + V_{\text{ref}}^\lambda(\zeta, \eta_{\lambda i}^0) \right) \phi_{v_\lambda}^{\lambda(m)} = \epsilon_{v_\lambda}^{\lambda(m)}(\eta_{\lambda i}^0) \phi_{v_\lambda}^{\lambda(m)} \quad (3.58)$$

with boundary conditions $\phi_{v_\lambda}^{\lambda(m)}(0) = \phi_{v_\lambda}^{\lambda(m)}(\zeta = \zeta_0) = 0$. The potential $V_{\text{ref}}^\lambda(\zeta, \eta_\lambda)$ is one of the reference potentials V_{ref}^λ defined in Sec. III.D.2 and III.D.3 but expressed in ζ , η_λ coordinates. Writing

$$F_{J J_\lambda}^{\lambda(m)} = \zeta^{-1/2} \sum_{v_\lambda} g_{J v_\lambda J_\lambda}^{\lambda(m)}(\eta_\lambda; \eta_{\lambda i}^0) \phi_{v_\lambda}^{\lambda(m)}(\zeta; \eta_{\lambda i}^0), \quad (3.59)$$

the counterpart of Eq. (3.47) becomes

$$\frac{d^2 \mathbf{g}_J^{\lambda(m)\pm}}{d\eta_\lambda^2} = \mathbf{U}_J^{\lambda(m)}(\eta_\lambda; \eta_{\lambda i}^0) \mathbf{g}_J^{\lambda(m)\pm}, \quad (3.60)$$

where the effective potential matrix (again being physically dimensionless) is

$$\mathbf{U}_J^{\lambda(m)} = \zeta^2(\eta_{\lambda i}^0) \mathbf{U}_J^{\lambda(m)}(\eta_\lambda; \eta_{\lambda i}^0) \quad (3.61)$$

with

$$\mathbf{U}_J^{\lambda(m)}(\eta_\lambda; \eta_{\lambda i}^0) = -\mathbf{K}^{\lambda(m)2} + \mathbf{U}_J^{c\lambda(m)} + \mathbf{U}_J^{(m)} \quad (3.62)$$

The matrix $\zeta^2(\eta_{\lambda i}^0)$ is defined analogously to ρ_λ^2 of Eq. (3.49) with ρ_λ replaced by ζ and φ_λ by η_λ . The matrices $\mathbf{K}^{\lambda(m)2}$ and $\mathbf{U}_J^{(m)}$ are given by expressions similar to Eqs. (3.50) and (3.51), respectively, with the superscript (m) replacing (s) and appropriate coordinate changes made, while the centrifugal potential matrix is given by

$$[\mathbf{U}_J^{c\lambda(m)}(\eta_\lambda; \eta_{\lambda i}^0)]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \langle v_\lambda | \frac{j_\lambda^2 - \frac{1}{4}}{\zeta^2 \sin^2 \eta_\lambda} + \frac{(J - j_\lambda)^2 - \frac{1}{4}}{\zeta^2 \cos^2 \eta_\lambda} - \frac{1}{4\zeta^2} | v'_\lambda \rangle \delta_{j_\lambda j'_\lambda}. \quad (3.63)$$

Smooth transformation between subregions in Region IV involves Eqs. (3.41) with the overlap matrix \mathbf{S}_i^λ given by

$$[\mathbf{S}_i^\lambda(\eta_{\lambda i}^0)]_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \delta_{j_\lambda j'_\lambda} \langle \phi_{v_\lambda}^{\lambda(m)}(\zeta, \eta_{\lambda i+1}^0) | \phi_{v'_\lambda}^{\lambda(m)}(\zeta, \eta_{\lambda i}^0) \rangle, \quad (3.64)$$

and the transformation between Regions III and IV is achieved with equations

$$\mathbf{g}_J^{\lambda(m)\pm}(\eta_{\lambda 0}; \eta_{\lambda 1}^0) = \zeta^{1/2} \mathbf{g}_J^{\lambda(s)\pm}(\varphi_{\lambda 0}; \varphi_{\lambda n_{\text{III}}}^0) \quad (3.65a)$$

and

$$\frac{d\mathbf{g}_J^{\lambda(m)\pm}}{d\eta_\lambda}(\eta_{\lambda 0}; \eta_{\lambda 1}^0) = \zeta^{3/2} \frac{d\mathbf{g}_J^{\lambda(s)\pm}}{d\varphi_\lambda}(\varphi_{\lambda 0}; \varphi_{\lambda n_{\text{III}}}^0), \quad (3.65b)$$

where

$$(\zeta^b)_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda} = \delta_{j_\lambda j'_\lambda} \langle \phi_{v_\lambda}^{\lambda(m)}(\zeta; \eta_{\lambda 1}^0) | \left(\frac{\zeta}{\rho_{\lambda 0} - \zeta} \right)^b | \phi_{v'_\lambda}^{\lambda(s)}(\rho_{\lambda 0} - \zeta; \varphi_{\lambda n_{\text{III}}}^0) \rangle$$

$$b = \frac{1}{2}, \frac{3}{2}. \quad (3.66)$$

E. Integration of the Schrödinger equation

We generate solutions $\mathbf{g}_J^{\lambda+}$ and their derivatives with respect to the propagation variable by choosing at $R_\lambda = R'_{\lambda 0}$ arbitrary initial values for these two matrices and integrating numerically Eqs. (3.38), (3.47), and (3.60) from the beginning of Region II to the end of Region IV. Similarly, we generate the $\mathbf{g}_J^{\lambda-}$ solutions and their derivatives by choosing arbitrary initial values for these two matrices at $\eta_\lambda = \eta_{\lambda 1}$ and numerically integrating these equations from the end of Region IV to the beginning of Region II.

Any appropriate numerical procedure may be employed to integrate the coupled equations. The one we used, which is well suited to equations of the type of Eqs. (3.38), (3.47), and (3.60), is the one developed by Gordon.³⁵ In Region II, it can be applied without modification,³⁶ but in Regions III and IV, the nonsymmetric nature of the effective interaction potential matrices [Eqs. (3.48) and (3.61)] requires a short modification of the method. As formulated by Gordon, in propagating a system of coupled equations, a transformation to a representation in which the effective potential matrix (say \mathbf{U}) becomes diagonal is required. This necessitates finding the eigenvalues of \mathbf{U} . In the special case where \mathbf{U} is real and symmetric, these eigenvalues are real and the eigenvector matrix is orthogonal. This simplifies the calculation and allows for an efficient program. The effective potential matrices of Regions III and IV as given by Eqs. (3.48) and (3.61) are real but nonsymmetric and thus could have complex eigenvalues and eigenvectors. These potential matrices are, however, equal to the product of two symmetric matrices, one of which (ρ_λ^2 for Region III and ξ^2 for Region IV) is the matrix representation of a positive definite operator (ρ_λ^2 or ξ^2) and hence has positive definite eigenvalues. By using these special properties to define the "square root" of ρ_λ^2 and ξ^2 , it is shown in Appendix B that both the eigenvalues and eigenvectors of the effective potential matrix are always real but the eigenvector matrix is not generally orthogonal. This allows us to use real variables throughout the integration, with the only major program changes from the usual Gordon method being in the routines needed to find the eigenvalues and eigenvectors of the effective potential matrix, and in the manipulation of the eigenvector matrices.

F. Restrictions and limitations

We should at this point summarize the possible limitations and restrictions on the method other than those inherent in the numerical procedures involved or those arising from computer limitations.

First, the choice of matching surfaces in Eqs. (3.2) is largely determined by the shape of the potential energy surface in Fig. 2, and for many reactions, an efficient choice will require somewhat different matching planes. A change in the exact mathematical form of the matching surfaces can significantly affect the details of the integration in Region IV and in the matching procedure although the basic concepts will be preserved. In choosing the matching surfaces for a given reaction, primary consideration should be given to ob-

taining an efficient representation of the wavefunction in the vicinity of the matching surfaces. This requires us to avoid too large a potential anisotropy in the matching region, for in that case, our coupled-channel solution will require many closed rotational channels for convergence. At the same time, too small a potential anisotropy (resulting in considerable flux "leakage" through $\gamma_\lambda = \pi/2$ configurations in the matching region) can result in poor convergence of the matching procedure (as will be discussed in Sec. IV). One therefore needs to be clever in choosing these surfaces, and it is possible that for certain reactions, no choice satisfies all of the above criteria and simultaneously leads to a mathematically tractable matching procedure.

One case where the choice of surfaces specified by Eqs. (3.2) leads to a set of coupled equations in the matching region [Eqs. (3.60)], which is not easily solved without including a large number of closed rotational channels, is when $\alpha_{\nu\lambda}$ (or $\alpha_{\kappa\lambda}$) $\geq 3\pi/4$. [See Eq. (A3) for the definition of these angles.] The reason for this is that when this inequality is satisfied, integration in the matching region will extend into those regions of configuration space for which r_ν (or r_κ) = 0, and hence will sample the very high potential energy in those configurations [for which $\gamma_\lambda = 0$ (or π)] while possibly sampling low potential energy for other configurations (near $\gamma_\lambda = \pi/2$). That this is the case can be verified by noting that during the integration in the matching region, η_λ must scan the range from $(\pi - \alpha_{\nu\lambda})/2$ to $\pi/4$ [from Eqs. (3.14), (3.15), and (3.17)] and that Eq. (A5) yields $r_\nu = 0$ when $\gamma_\lambda = 0$ and $\alpha_{\nu\lambda} \geq 3\pi/4$ at some η_λ within this range. From Eqs. (A3) we note that $\alpha_{\nu\lambda} \geq 3\pi/4$ implies $m_\kappa(m_\lambda + m_\nu + m_\kappa) < m_\lambda m_\nu$, so that this restriction applies primarily to reactions with one atom of the triatomic system considerably lighter than the other two. We should also point out that this problem can be eliminated by the use of a different coordinate system in the matching region or by the use of "rotationally adiabatic" rotational basis functions [rather than $\varphi_{J_\lambda}(\gamma_\lambda)$].

When one of the three arrangement channels is closed, the method must be somewhat modified,²¹ but this is not a complication. Other practical limitations to the method occur for reactions where break-up collisions are allowed or for which virtual excitations to closed dissociative channels influence the other reactive and nonreactive processes significantly. The present method is not capable of treating any dissociation process, but this is not a serious limitation for many reactions at energies of chemical interest. A more general method which utilizes generalized hyperspherical functions is currently being developed in these laboratories for the purpose of treating both break-up and rearrangement collisions.

IV. THE MATCHING

A. Projection of the wavefunction onto the matching surface basis functions

At the completion of the integration in arrangement channel region λ , we have generated solutions which satisfy the Schrödinger equation in that region, but which do not, in general, match smoothly with the cor-

responding wavefunctions obtained from the integrations in the other arrangement channel regions ν and κ . In this section we describe the procedure for accomplishing this smooth matching. This procedure may conveniently be broken up into two parts. First, we consider the projection of the full wavefunction and its derivative normal to the matching surface onto a set of orthonormal basis functions which span the matching surfaces. Second, we take linear combinations of the wavefunctions in each arrangement channel region and match them smoothly, on these surfaces, to linear combinations of the corresponding wavefunctions in the other arrangement channel regions. The resulting matrix equations can be solved to yield a set of solutions which satisfy Condition (a) of Sec. II. A and can subsequently (see Sec. V. A) be used to form the scattering solutions satisfying Condition (c) of that section.

Let us consider the projection procedure for the matching surface $\pi_{\nu\lambda}$ [Fig. 2(a)]. The analogous equations for $\pi_{\kappa\nu}$ and $\pi_{\lambda\kappa}$ are obtained from those derived below by cyclic permutation of the indices $\lambda\nu\kappa$. We first consider the wavefunction on $\pi_{\nu\lambda}$ obtained from the integration in arrangement channel λ . Using Eqs. (3.59), (3.5), (2.13), and (2.10), we get the following expression for the wavefunction in Region IV (Subregion i):

$$\Psi_J^{\lambda\nu j' \lambda^*}(\theta_\lambda, \zeta, \eta_\lambda, \gamma_\lambda) = \frac{\sqrt{2}\varphi_J(\theta_\lambda)}{\zeta^{3/2}(\sin 2\eta_\lambda)^{1/2}} \left(\sum_{\nu_\lambda j_\lambda} \varphi_{j_\lambda}(\gamma_\lambda) \phi_{\nu_\lambda}^\lambda(\zeta; \eta_{\lambda i}^0) g_{J\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}(\eta_\lambda; \eta_{\lambda i}^0) \right). \quad (4.1)$$

Throughout Sec. IV we will consider superscript (m) of Sec. III. D. 4 to be present implicitly and will omit writing it explicitly. We have, however, added the indices $\nu_\lambda j'_\lambda$ to denote different linearly independent solutions obtained by using different initial conditions in the numerical solution of the Schrödinger equation. As explained in Sec. III. D. 1, if we truncate the close coupling expansion after N vibration-rotation basis functions, there will be N sets of indices $\nu_\lambda j'_\lambda$ in Eq. (4.1).

The expression in large parentheses in Eq. (4.1) is expanded in terms of a different set of vibrational functions $\phi_{\nu_\lambda}^\lambda(\zeta; \eta_{\lambda i}^0)$ for each subregion i of Region IV. We now transform to a representation in terms of a single set of vibration-rotation basis functions $\varphi_{j_\lambda}(\gamma_\lambda) \phi_{\nu_\lambda}^\lambda(\zeta)$ for all of Region IV. The actual functions $\phi_{\nu_\lambda}^\lambda(\zeta)$ to be used are arbitrary, but for reactions such as $H + H_2$ which favor reaction through collinear geometries, the most efficient set for this purpose (as will be explained in more detail below) are the functions $\phi_{\nu_\lambda}^\lambda(\zeta; \eta_{\lambda 0})$ defined along the cut $\eta_\lambda = \eta_{\lambda 0}$, and which will be denoted by $\phi_{\nu_\lambda}^\lambda(\zeta)$ simply. The transformation equations associated with the change in the vibrational basis set are given by equations similar to Eqs. (3.41) and (3.53), where a different overlap matrix will be generated for each subregion i . We will denote the new "g" function thus obtained by $g_{J\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}(\eta_\lambda)$ (we will omit the parameter $\eta_{\lambda 0}$). With this change of vibrational basis, we can write a single expression for $\Psi_J^{\lambda\nu j' \lambda^*}$ valid throughout all of Region IV:

$$\Psi_J^{\lambda\nu j' \lambda^*}(\theta_\lambda, \zeta, \eta_\lambda, \gamma_\lambda) = \frac{\sqrt{2}\varphi_J(\theta_\lambda)}{\zeta^{3/2}(\sin 2\eta_\lambda)^{1/2}} \Phi_J^{\lambda\nu j' \lambda^*}(\zeta, \eta_\lambda, \gamma_\lambda), \quad (4.2)$$

where

$$\Phi_J^{\lambda\nu j' \lambda^*} = \sum_{\nu_\lambda j_\lambda} \varphi_{j_\lambda}(\gamma_\lambda) \phi_{\nu_\lambda}^\lambda(\zeta) g_{J\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}(\eta_\lambda). \quad (4.3)$$

On the matching surface $\pi_{\nu\lambda}$, η_λ and γ_λ are related to each other by the equation [from Eqs. (A14) and (3.18)]

$$\cot 2\eta_\lambda = -\cot \alpha_{\nu\lambda} \cos \gamma_\lambda, \quad 0 \leq \gamma_\lambda \leq \frac{\pi}{2} \text{ and } \frac{3\pi}{2} \leq \gamma_\lambda < 2\pi. \quad (4.4)$$

Hence, if we substitute $\eta_\lambda(\gamma_\lambda)$ as obtained from Eq. (4.4) into Eqs. (4.2) and (4.3), we obtain the desired wavefunction on $\pi_{\nu\lambda}$.

In order to insure a smooth matching of the wavefunctions, we need also to match the derivative of the wavefunction of Eqs. (4.2) and (4.3) at the matching surfaces. Although many types of derivatives are possible, the normal derivative $\partial/\partial n_{\nu\lambda}$ to the matching half-plane possesses many useful mathematical properties (some of which are seen below), and for this reason we will consider it in the following discussion. Expressions for $\partial/\partial n_{\nu\lambda}$ in terms of ζ , η_λ , and γ_λ are derived in Appendix A [Eq. (A18)]. Since these are internal configuration coordinates (i.e., those on which V^λ depends) we are free to choose any one external variable (such as θ_λ or θ_ν) to hold constant during the differentiation process. We must, however, use this same variable in deriving all equations concerning the derivative matching on $\pi_{\nu\lambda}$. Choosing this external variable to be θ_λ and introducing Eq. (A18) into Eqs. (4.2) and (4.3), and then using Eq. (4.4) to express everything on the matching surface, we obtain

$$\frac{\partial \Psi_J^{\lambda\nu j' \lambda^*}}{\partial n_{\nu\lambda}} = \frac{\sqrt{2}\varphi_J(\theta_\lambda) \sin \alpha_{\nu\lambda}}{\zeta^{5/2}(\sin 2\eta_\lambda)^{3/2}} \Phi_J^{\lambda\nu j' \lambda^*}(\zeta, \gamma_\lambda), \quad (4.5)$$

where

$$\begin{aligned} \Phi_J^{\lambda\nu j' \lambda^*}(\zeta, \gamma_\lambda) &= \sum_{\nu_\lambda j_\lambda} \phi_{\nu_\lambda}^\lambda(\zeta) \varphi_{j_\lambda}(\gamma_\lambda) \left(\frac{1}{2} \frac{dg_{J\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}}{d\eta_\lambda} + \cot \alpha_{\nu\lambda} \left(\frac{1}{2} \cos \gamma_\lambda \right. \right. \\ &\quad \left. \left. + i j_\lambda \sin \gamma_\lambda \right) g_{J\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}(\eta_\lambda(\gamma_\lambda)) \right). \end{aligned} \quad (4.6)$$

The derivative $dg/d\eta_\lambda$ must be evaluated by allowing η_λ to be independent of γ_λ before the expression $\eta_\lambda = \eta_\lambda(\gamma_\lambda)$ given by Eq. (4.4) is used.

We now wish to expand the functions $\Phi_J^{\lambda\nu j' \lambda^*}$ and $\Phi_J^{\lambda\nu j' \lambda^*}$ on the matching surface $\pi_{\nu\lambda}$ in terms of a set of basis functions $B_{\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}$ which span that surface, ζ and γ_λ being the independent variables. We choose the $B_{\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}$ to be

$$B_{\nu_\lambda j_\lambda}^{\lambda\nu j' \lambda^*}(\zeta, \gamma_\lambda) = \phi_{\nu_\lambda}^\lambda(\zeta) A_{j_\lambda}^{\nu_\lambda j' \lambda^*}(\gamma_\lambda), \quad (4.7)$$

where the $\phi_{\nu_\lambda}^\lambda$'s were defined above [in the paragraph preceding Eq. (4.2)], and the $A_{j_\lambda}^{\nu_\lambda j' \lambda^*}(\gamma_\lambda)$ are a set of rotational functions which we shall require to be orthonormal and complete on the domain $0 \leq \gamma_\lambda \leq \frac{1}{2}\pi$, $\frac{1}{2}3\pi \leq \gamma_\lambda < 2\pi$. For convenience, we will also impose the condition that $A_{j_\lambda}^{\nu_\lambda j' \lambda^*}(\gamma_\lambda)$ be real and that

$$A_{j_\lambda}^{\nu\lambda}(\gamma_\lambda) = (-1)^{j_\lambda} A_{j_\lambda}^{\nu\lambda}(2\pi - \gamma_\lambda). \quad (4.8)$$

This is not a significantly restrictive assumption, and will lead to matching equations involving only real quantities.

The crucial characteristic in our choice of the rotational basis functions A is that they be complete for the domain $0 \leq \gamma_\lambda \leq \frac{1}{2}\pi$, $\frac{1}{2}3\pi \leq \gamma_\lambda < 2\pi$. This contrasts with the 0 to 2π interval over which the asymptotic rotational functions $\phi_{j_\lambda}(\gamma_\lambda)$ are complete. What we have actually done is to divide the domain of γ_λ into two equal subdomains: (a) 0 to $\frac{1}{2}\pi$ and $\frac{1}{2}3\pi$ to 2π , on which we choose the $\pi_{\nu\lambda}$ rotational functions $A_{j_\lambda}^{\nu\lambda}(\gamma_\lambda)$, and (b) $\frac{1}{2}\pi$ to $\frac{1}{2}3\pi$, where we use the analogous functions $A_{j_\lambda}^{\lambda\kappa}(\gamma_\lambda)$ which span $\pi_{\lambda\kappa}$. The union $A_{j_\lambda}^{\lambda}(\gamma_\lambda)$ of the two sets of functions $\{A_{j_\lambda}^{\nu\lambda}, A_{j_\lambda}^{\lambda\kappa}\}$ forms a set of rotational functions which spans $(0, 2\pi)$ and this allows us to establish a one-to-one correspondence between the rotational functions $A_{j_\lambda}^{\lambda}$ which span the pair of matching surfaces $\pi_{\nu\lambda}$ and $\pi_{\lambda\kappa}$, and the asymptotic functions $\phi_{j_\lambda}^{\lambda}(\gamma_\lambda)$. More specifically, if we have N vibration-rotation basis functions asymptotically in arrangement channel λ , the sum of the number of $B^{\nu\lambda}$ and $B^{\lambda\kappa}$ functions must be N . For a symmetric reaction (i. e., one in which channels ν and κ are equivalent), we must use $N/2$ functions in each of these two sets. In this case, the rotational quantum numbers j_λ spanned by the $B_{\nu\lambda j_\lambda}^{\nu\lambda}$ (for each vibrational quantum number ν_λ) include only one-half of those spanned by the asymptotic functions ϕ_{j_λ} . The number of the latter should in such cases be even, which is not a severe constraint.

We now discuss possible choices for the functions $A_{j_\lambda}^{\nu\lambda}$. Two sets of functions which are both orthonormal and complete over the range $0 \leq \gamma_\lambda \leq \frac{1}{2}\pi$ and $\frac{1}{2}3\pi \leq \gamma_\lambda < 2\pi$ are $(\pi)^{-1/2} \exp(2ij_\lambda \gamma_\lambda)$ and $(\pi)^{-1/2} \exp[(2j_\lambda + 1)i\gamma_\lambda]$ for $j_\lambda = 0, \pm 1, \pm 2, \dots$. These do not satisfy the condition of Eq. (4.8), but certain linear combinations of them do such as (a) $(\pi)^{-1/2}$, $(2/\pi)^{1/2} \cos 2\gamma_\lambda$, $(2/\pi)^{1/2} \sin 2\gamma_\lambda$, $(2/\pi)^{1/2} \cos 4\gamma_\lambda$, $(2/\pi)^{1/2} \sin 4\gamma_\lambda$, ..., and (b) $(2/\pi)^{1/2} \sin \gamma_\lambda$, $(2/\pi)^{1/2} \cos \gamma_\lambda$, $(2/\pi)^{1/2} \sin 3\gamma_\lambda$, $(2/\pi)^{1/2} \cos 3\gamma_\lambda$, ... We can also choose mixtures of (a) and (b) above such as (c) $(2/\pi)^{1/2} \cos \gamma_\lambda$, $(2/\pi)^{1/2} \sin 2\gamma_\lambda$, $(2/\pi)^{1/2} \cos 3\gamma_\lambda$, ... This last set of functions (corresponding to $j_\lambda = 0, 1, 2, \dots$, respectively) has the property that all its members vanish at $\gamma_\lambda = \pi/2$ and $3\pi/2$. This makes these functions very efficient for expanding the wavefunctions for certain reactions, as described below. An alternative to analytical functions would be a numerically determined set such as the rotational eigenfunctions for some approximate potential on the matching surface. To see what these functions might look like for $H + H_2$, in Fig. 6 we plot contours of the Porter-Karplus potential³¹ on the two-dimensional matching half-plane $\pi_{\nu\lambda}$. The lines converging at the origin are intersections of $\pi_{\nu\lambda}$ with $\gamma_\lambda = \text{constant}$ planes and correspond therefore to constant values of η_λ . The figure indicates that only the region of the matching surface for which γ_λ is in the range $0-60^\circ$ and $300^\circ-360^\circ$ (and η_λ in the range $\eta_{\lambda 0} = 30^\circ-36.9^\circ$) has a low enough potential energy to contribute significantly to the reaction at energies less than 1 eV. This implies that we should choose a basis set $B^{\nu\lambda}$ which describes the wavefunction best near

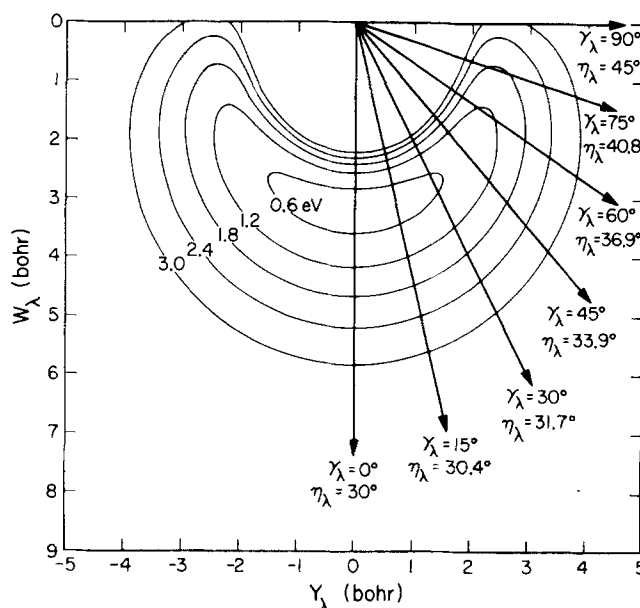


FIG. 6. Plot of equipotential contours on the matching surface $\pi_{\nu\lambda}$ for the $H + H_2$ reaction in the Cartesian coordinate system W_λ, Y_λ , where $W_\lambda = (X_\lambda^2 \sin^2 \alpha_{\nu\lambda} + Z_\lambda^2 \cos^2 \alpha_{\nu\lambda})^{1/2}$ and the system $X_\lambda, Y_\lambda, Z_\lambda$ is the one described in Sec. III.A. Because of the symmetry of the H_3 system, Fig. 6 is equivalent to the lower half of Fig. 2(c) since the $Z_\lambda < 0$ half-plane of the $OY_\lambda Z_\lambda$ plane is for this system the same as the $\pi_{\kappa\nu}$ matching plane. The half-lines emanating from the origin correspond to constant values of γ_λ and η_λ , as indicated. To each such half-line, for which $\gamma_\lambda = \bar{\gamma}_\lambda$, there corresponds a symmetric one with respect to the vertical axis, having the same value of η_λ and a value of $\gamma_\lambda = 360^\circ - \bar{\gamma}_\lambda$ in the 270° to 360° range.

$\gamma_\lambda = 0$, i. e., near $\eta_\lambda = \eta_{\lambda 0}$. For this reason, we previously chose the vibrational eigenfunctions $\phi_{\nu_\lambda}^{\lambda}(\xi)$ to be solutions to Eq. (3.5) for $\eta_\lambda = \eta_{\lambda 0}$. [See paragraph preceding Eq. (4.2)]. Although there is no single γ_λ -dependent rotational potential which describes the rotational motion on the matching surface correctly for all ξ , it should be clear from Fig. 6 that rotational functions which are numerically determined from the potential on the matching surface for a fixed ξ (such as the ξ for which this potential, at $\gamma_\lambda = 0$, has a minimum) will be localized near $\gamma_\lambda = 0$ and must be close to zero near $\gamma_\lambda = \pi/2$ and $3\pi/2$. For this reason, the analytical set (c) should be efficient for expanding the wavefunction on $\pi_{\nu\lambda}$. Finally, we should mention that an important test of the correctness of the method is to demonstrate the invariance of the final converged results with respect to the choice of $A_{j_\lambda}^{\lambda}$.

We now expand the functions $\Phi_{j_\lambda}^{\nu\lambda j_\lambda' \pm}$ and $\Phi_{j_\lambda}^{\lambda\kappa j_\lambda' \pm}$ [defined by Eqs. (4.3) and (4.6)] in terms of the matching surface functions $B_{\nu\lambda j_\lambda}^{\nu\lambda}$ as follows:

$$\Phi_{j_\lambda}^{\lambda\nu j_\lambda' \pm} = \sum_{\nu_\lambda j_\lambda} \bar{h}_{\nu_\lambda j_\lambda}^{\lambda\nu j_\lambda' \pm} B_{\nu\lambda j_\lambda}^{\nu\lambda}(\xi, \gamma_\lambda), \quad (4.9)$$

$$\Phi_{j_\lambda}^{\lambda\kappa j_\lambda' \pm} = \sum_{\nu_\lambda j_\lambda} \bar{h}_{\nu_\lambda j_\lambda}^{\lambda\kappa j_\lambda' \pm} B_{\nu\lambda j_\lambda}^{\nu\lambda}(\xi, \gamma_\lambda). \quad (4.10)$$

Whereas the indices $\nu_\lambda j_\lambda'$ assume N values, $\nu_\lambda j_\lambda$ assume fewer values than that. In view of our previous discussion, $N/2$ is a convenient choice for this number for

the highly symmetric H_3 system. The coefficients $\bar{h}_{j\nu\lambda}^{\lambda\nu j'j' \pm}$ and $\bar{h}_{j\nu\lambda}^{\lambda\nu j'j' \pm}$ may be found by equating Eq. (4.3) on $\pi_{\nu\lambda}$ with Eq. (4.9), and Eq. (4.6) with Eq. (4.10), multiplying the resulting expressions by $B_{\nu\lambda}^{*j'j'}$, and integrating them over ξ and γ_λ . Using the orthonormality of the $B_{\nu\lambda}^{j'j'}$ functions on the matching surface and Eq. (4.8), and interchanging in the end the $\nu_\lambda j_\lambda$ indices with the $\nu_\lambda j_\lambda$ ones, we get

$$\bar{h}_{j\nu\lambda}^{\lambda\nu j'j' \pm} = \sqrt{\frac{2}{\pi}} \sum_{j'_\lambda} \int_0^{\pi/2} d\gamma_\lambda A_{j'_\lambda}^{\nu\lambda}(\gamma_\lambda) g_{j\nu\lambda}^{\lambda\nu j'j' \pm}[\eta_\lambda(\gamma_\lambda)] \left\{ \begin{matrix} \cos j'_\lambda \gamma_\lambda \\ i \sin j'_\lambda \gamma_\lambda \end{matrix} \right\}, \quad (4.11)$$

$$\begin{aligned} \bar{h}_{j\nu\lambda}^{\lambda\nu j'j' \pm} = \frac{1}{\sqrt{2\pi}} \sum_{j'_\lambda} \int_0^{\pi/2} d\gamma_\lambda A_{j'_\lambda}^{\nu\lambda}(\gamma_\lambda) \left\{ d g_{j\nu\lambda}^{\lambda\nu j'j' \pm}[\eta_\lambda(\gamma_\lambda)] / d\eta_\lambda \right. \\ \times \left(\begin{matrix} \cos j'_\lambda \gamma_\lambda \\ i \sin j'_\lambda \gamma_\lambda \end{matrix} \right) + \cot \alpha_{\nu\lambda} \left[\left(j'_\lambda + \frac{1}{2} \right) \left(\begin{matrix} \cos(j'_\lambda + 1) \gamma_\lambda \\ i \sin(j'_\lambda + 1) \gamma_\lambda \end{matrix} \right) \right. \\ \left. - \left(j'_\lambda - \frac{1}{2} \right) \left(\begin{matrix} \cos(j'_\lambda - 1) \gamma_\lambda \\ i \sin(j'_\lambda - 1) \gamma_\lambda \end{matrix} \right) \right] g_{j\nu\lambda}^{\lambda\nu j'j' \pm}[\eta_\lambda(\gamma_\lambda)] \left. \right\}, \end{aligned} \quad (4.12)$$

where the upper term in the large parentheses is to be used for even j_λ , and the lower for odd j_λ , and use was made of Eq. (4.8).

We now must consider the expansion of the wavefunction obtained from the integration in channel ν , in the same matching surface basis functions $B_{\nu\lambda}^{j'j'}$ of Eq. (4.7). To do this we first express the wavefunction and its normal derivative in a form analogous to Eqs. (4.2), (4.3), (4.5), and (4.6). For the wavefunction we get

$$\Psi_J^{\nu\nu j'j' \pm} = \frac{\sqrt{2} \varphi_J(\theta_\nu)}{\xi^{3/2} (\sin 2\eta_\nu)^{1/2}} \Phi_J^{\nu\nu j'j' \pm}(\xi, \eta_\nu, \gamma_\nu), \quad (4.13)$$

where

$$\Phi_J^{\nu\nu j'j' \pm} = \sum_{\nu_\nu j_\nu} \varphi_{j_\nu}(\gamma_\nu) \phi_{\nu_\nu}^{\nu}(\xi) g_{j\nu\lambda}^{\nu\nu j'j' \pm}(\eta_\nu). \quad (4.14)$$

The vibrational basis function $\phi_{\nu_\nu}^{\nu}(\xi)$ is defined in a manner similar to $\phi_{\nu_\lambda}^{\lambda}(\xi)$ and, in fact, may be identical to it (for $\nu_\nu = \nu_\lambda$) if the reference potentials are defined appropriately. In terms of the ν arrangement channel coordinates, the relation between η_ν and γ_ν on the matching surface $\pi_{\nu\lambda}$ is given by

$$\cot 2\eta_\nu = \cot \alpha_{\nu\lambda} \cos \gamma_\nu, \quad \frac{1}{2}\pi \leq \gamma_\nu \leq \frac{3}{2}\pi. \quad (4.15)$$

This is easily derived from Eq. (4.4), using the relations (A12) and (A15) of the Appendix and Eq. (3.18).

In calculating the normal derivative of the wavefunc-

tion of Eq. (4.13) on the matching surface $\pi_{\nu\lambda}$, we must remember that θ_λ must be held constant during the differentiation. It is therefore desirable to express θ_ν in terms of θ_λ ,

$$\theta_\nu = \theta_\lambda + \Delta_{\nu\lambda}, \quad (4.16)$$

where $\Delta_{\nu\lambda}$ is a function of the internal variables R_λ, r_λ , γ_λ only as seen in Eqs. (A9) of the Appendix. If we express those two equations in terms of the variables ξ, η_λ , and γ_λ , then find the normal derivative of $\Delta_{\nu\lambda}$ using Eq. (A18) and finally use Eq. (4.4) to express all quantities on the matching surface $\pi_{\nu\lambda}$, we obtain the very useful equation valid only on this surface:

$$\frac{\partial \Delta_{\nu\lambda}}{\partial n_{\nu\lambda}}(\xi, \eta_\lambda, \gamma_\lambda) = 0. \quad (4.17)$$

As a consequence of this simplification, we can express the normal derivative of the wavefunction in arrangement channel ν on $\pi_{\nu\lambda}$ by

$$\frac{\partial \Psi_J^{\nu\nu j'j' \pm}}{\partial n_{\nu\lambda}} = \frac{\sqrt{2} \varphi_J(\theta_\lambda) e^{iJ\Delta_{\nu\lambda}}}{\xi^{5/2} (\sin 2\eta_\nu)^{3/2}} \Phi_J^{\nu\nu j'j' \pm}(\xi, \gamma_\nu), \quad (4.18)$$

where

$$\begin{aligned} \Phi_J^{\nu\nu j'j' \pm}(\xi, \gamma_\nu) = \sum_{j_\nu \nu_\nu} \varphi_{j_\nu}(\gamma_\nu) \phi_{\nu_\nu}^{\nu}(\xi) \left[\frac{1}{2} \left(\frac{d g_{j\nu\lambda}^{\nu\nu j'j' \pm}}{d\eta_\nu} \right)_{\eta_\nu=\eta_\nu(\gamma_\nu)} \right. \\ \left. - \cot \alpha_{\nu\lambda} \left(\frac{1}{2} \cos \gamma_\nu + i j_\nu \sin \gamma_\nu \right) g_{j\nu\lambda}^{\nu\nu j'j' \pm}[\eta_\nu(\gamma_\nu)] \right]. \end{aligned} \quad (4.19)$$

We now expand the functions $\Phi_J^{\nu\nu j'j' \pm}$ and $\Phi_J^{\nu\nu j'j' \pm}$ in terms of the matching surface functions $B_{\nu\lambda}^{j'j'}$ of Eq. (4.7). Note that we use the λ arrangement channel variables to express the ν arrangement channel wavefunction, using the transformation equations (A12), (A14), and (3.18) to relate the λ and ν sets of variables. The resulting expansions are

$$\Phi_J^{\nu\nu j'j' \pm}(\xi, \gamma_\lambda) = \sum_{\nu_\nu j_\nu} \bar{f}_{j\nu\lambda}^{\nu\nu j'j' \pm} B_{\nu\lambda}^{j'j'}(\xi, \gamma_\lambda), \quad (4.20)$$

$$\Phi_J^{\nu\nu j'j' \pm}(\xi, \gamma_\lambda) = \sum_{\nu_\nu j_\nu} \bar{f}_{j\nu\lambda}^{\nu\nu j'j' \pm} B_{\nu\lambda}^{j'j'}(\xi, \gamma_\lambda), \quad (4.21)$$

where the expansion coefficients are given by

$$\begin{aligned} \bar{f}_{j\nu\lambda}^{\nu\nu j'j' \pm} = \sqrt{\frac{2}{\pi}} \int_0^{\pi/2} d\gamma_\lambda \sum_{\nu'_\nu j'_\nu} (-1)^{j'_\nu} S_{\nu_\nu \nu'_\nu}^{\nu\lambda} A_{j'_\nu}^{\nu\lambda}(\gamma_\lambda) \\ \times g_{j\nu\lambda}^{\nu\nu j'j' \pm}[\eta_\nu(\gamma_\nu)] \left\{ \begin{matrix} \cos j'_\nu \gamma_\lambda \\ i \sin j'_\nu \gamma_\lambda \end{matrix} \right\}, \end{aligned} \quad (4.22)$$

$$\begin{aligned} \bar{f}_{j\nu\lambda}^{\nu\nu j'j' \pm} = -\frac{1}{\sqrt{2\pi}} \int_0^{\pi/2} d\gamma_\lambda \sum_{\nu'_\nu j'_\nu} (-1)^{j'_\nu} S_{\nu_\nu \nu'_\nu}^{\nu\lambda} A_{j'_\nu}^{\nu\lambda}(\gamma_\lambda) \left\{ \left(\frac{d g_{j\nu\lambda}^{\nu\nu j'j' \pm}}{d\eta_\nu} \right)_{\eta_\nu=\eta_\nu(\gamma_\nu)} \left(\begin{matrix} \cos j'_\nu \gamma_\lambda \\ -i \sin j'_\nu \gamma_\lambda \end{matrix} \right) \right. \\ \left. + \cot \alpha_{\nu\lambda} \left[\left(j'_\nu + \frac{1}{2} \right) \left(\begin{matrix} \cos(j'_\nu + 1) \gamma_\lambda \\ -i \sin(j'_\nu + 1) \gamma_\lambda \end{matrix} \right) - \left(j'_\nu - \frac{1}{2} \right) \left(\begin{matrix} \cos(j'_\nu - 1) \gamma_\lambda \\ -i \sin(j'_\nu - 1) \gamma_\lambda \end{matrix} \right) \right] g_{j\nu\lambda}^{\nu\nu j'j' \pm}[\eta_\nu(\gamma_\nu)] \right\}, \end{aligned} \quad (4.23)$$

where

$$S_{\nu\nu'}^{\nu\lambda} = \int_0^\infty \phi_{\nu\nu'}^\lambda(\xi) \phi_{\nu\nu'}^\nu(\xi) d\xi. \quad (4.24)$$

As before, the upper term in the large parentheses is used for even j_ν and the lower for odd j_ν .

B. The matching equations

With the wavefunctions from the integrations in both channels ν and λ expressed in terms of the basis set $B_{\nu\lambda j_\lambda}^{\nu\lambda}(\xi, \gamma_\lambda)$ on $\pi_{\nu\lambda}$, we can now take the appropriate linear combinations of these solutions to yield solutions to the full Schrödinger equation which are continuous and smooth throughout all of configuration space. Let us denote the fully matched solutions thus obtained by $\Psi_j^{(i)vj}$. There are N sets of indices v, j , and the superscript (i) can have the values 1, 2, or 3. The full set of indices $(i)vj$ thus scans $3N$ values, and we will therefore obtain $3N$ linearly independent solutions to the Schrödinger equation.³⁷

We now write $\Psi_j^{(i)vj}$ in terms of the solutions $\Psi_j^{\lambda\nu\nu\lambda j_\lambda^\pm}$ and also in terms of the $\Psi_j^{\nu\nu\nu\nu j_\nu^\pm}$:

$$\begin{aligned} \Psi_j^{(i)vj} &= \sum_{\nu_\lambda j_\lambda'} \left(\Psi_j^{\lambda\nu_\lambda j_\lambda'^+} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj+} + \Psi_j^{\lambda\nu_\lambda j_\lambda'^-} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj-} \right) \\ &= \sum_{\nu_\nu j_\nu'} \left(\Psi_j^{\nu\nu_\nu j_\nu'^+} C_{j\nu\nu_\nu j_\nu'}^{(i)vj+} + \Psi_j^{\nu\nu_\nu j_\nu'^-} C_{j\nu\nu_\nu j_\nu'}^{(i)vj-} \right) \end{aligned} \quad (4.25)$$

and

$$\begin{aligned} \frac{\partial \Psi_j^{(i)vj}}{\partial n_{\nu\lambda}} &= \sum_{\nu_\lambda j_\lambda'} \left(\frac{\partial \Psi_j^{\lambda\nu_\lambda j_\lambda'^+}}{\partial n_{\nu\lambda}} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj+} + \frac{\partial \Psi_j^{\lambda\nu_\lambda j_\lambda'^-}}{\partial n_{\nu\lambda}} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj-} \right) \\ &= \sum_{\nu_\nu j_\nu'} \left(\frac{\partial \Psi_j^{\nu\nu_\nu j_\nu'^+}}{\partial n_{\nu\lambda}} C_{j\nu\nu_\nu j_\nu'}^{(i)vj+} + \frac{\partial \Psi_j^{\nu\nu_\nu j_\nu'^-}}{\partial n_{\nu\lambda}} C_{j\nu\nu_\nu j_\nu'}^{(i)vj-} \right). \end{aligned} \quad (4.26)$$

The coefficients $C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj\pm}$ and $C_{j\nu\nu_\nu j_\nu'}^{(i)vj\pm}$ are to be determined by applying these two sets of equations on $\pi_{\nu\lambda}$ (and similar equations on $\pi_{\kappa\nu}$ and $\pi_{\lambda\kappa}$), and by imposing the scattering solution boundary conditions as explained in Sec. V.A. Equations (4.25) and (4.26), when evaluated on $\pi_{\nu\lambda}$, comprise the smooth matching conditions.

By substituting Eqs. (4.2), (4.13), and (4.16) into Eqs. (4.25), we obtain the following expression:

$$\begin{aligned} &\sum_{\nu_\lambda j_\lambda'} \left(\Phi_j^{\lambda\nu_\lambda j_\lambda'^+} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj+} + \Phi_j^{\lambda\nu_\lambda j_\lambda'^-} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj-} \right) \\ &= e^{iJ\Delta_{\nu\lambda}} \sum_{\nu_\nu j_\nu'} \left(\Phi_j^{\nu\nu_\nu j_\nu'^+} C_{j\nu\nu_\nu j_\nu'}^{(i)vj+} + \Phi_j^{\nu\nu_\nu j_\nu'^-} C_{j\nu\nu_\nu j_\nu'}^{(i)vj-} \right). \end{aligned} \quad (4.27)$$

The analogous expression for the normal derivatives is obtained from Eq. (4.27) by replacing the Φ by the Φ' in that equation. If we now substitute the expansions given by Eqs. (4.9), (4.10), (4.20), and (4.21) into Eq. (4.27) and into its equivalent for the normal derivatives, then multiply through by $B_{\nu\lambda j_\lambda}^{\nu\lambda}(\xi, \gamma_\lambda)$, and integrate over ξ and γ_λ , we obtain the following system of linear algebraic equations:

$$\sum_{\nu_\lambda j_\lambda'} \left(\bar{h}_{\nu\lambda j_\lambda}^{\lambda\nu_\lambda j_\lambda'^+} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj+} + \bar{h}_{\nu\lambda j_\lambda}^{\lambda\nu_\lambda j_\lambda'^-} C_{j\lambda\nu_\lambda j_\lambda'}^{(i)vj-} \right)$$

$$= \sum_{\nu_\nu j_\nu'} \left(\bar{s}_{\nu\lambda}^J \right)_{\nu_\lambda j_\lambda}^{\nu_\nu j_\nu} \sum_{\nu_\nu j_\nu'} \left(\bar{f}_{\nu\nu_\nu j_\nu'}^{\nu\nu_\nu j_\nu'^+} C_{j\nu\nu_\nu j_\nu'}^{(i)vj+} + \bar{f}_{\nu\nu_\nu j_\nu'}^{\nu\nu_\nu j_\nu'^-} C_{j\nu\nu_\nu j_\nu'}^{(i)vj-} \right), \quad (4.28)$$

with the analogous equation for derivatives obtained by using \bar{h}' and \bar{f}' instead of \bar{h} and \bar{f} above. The matrix $\bar{s}_{\nu\lambda}^J$ is defined by

$$\left(\bar{s}_{\nu\lambda}^J \right)_{\nu_\lambda j_\lambda}^{\nu_\nu j_\nu} = \delta_{\nu_\lambda j_\lambda}^{\nu_\nu j_\nu} \begin{cases} 2 \int_0^{\pi/2} A_{j_\lambda}^{\nu_\lambda} A_{j_\nu}^{\nu_\lambda} \cos J \Delta_{\nu\lambda} d\gamma_\lambda & \text{for } j_\lambda + j_\nu = \text{even} \\ 2i \int_0^{\pi/2} A_{j_\lambda}^{\nu_\lambda} A_{j_\nu}^{\nu_\lambda} \sin J \Delta_{\nu\lambda} d\gamma_\lambda & \text{for } j_\lambda + j_\nu = \text{odd} \end{cases}, \quad (4.29)$$

or, by the expression (which is only equivalent to it for a complete set of functions $B^{\nu\lambda}$)

$$\bar{s}_{\nu\lambda}^J = \exp(iJ \Delta^{\nu\lambda}), \quad (4.30)$$

where

$$(\Delta^{\nu\lambda})_{\nu_\lambda j_\lambda}^{\nu_\nu j_\nu} = \langle B_{\nu_\lambda j_\lambda}^{\nu\lambda} | \Delta_{\nu\lambda} | B_{\nu_\nu j_\nu}^{\nu\lambda} \rangle. \quad (4.31)$$

As should be evident from Eqs. (4.30) and (4.31), the matrix $\bar{s}_{\nu\lambda}^J$ is unitary since $\Delta_{\nu\lambda}$ is real, and therefore $\Delta^{\nu\lambda}$ is Hermitian.

By examining the definitions given in Eqs. (4.11), (4.12), (4.22), (4.23), and (4.29) for the various symbols used in Eq. (4.28) and its equivalent for the derivatives, we find that the latter set of equations involve either purely real terms or purely imaginary terms. Let us omit the factor i appearing in Eqs. (4.11), (4.12), (4.22), and (4.23) and replace it in Eq. (4.29) by $(-1)^{j_\nu}$. We denote all of the real coefficients thus obtained by removing the bars which previously appeared above their symbols. Equation (4.28) and its normal derivative counterpart continue to be valid for the unbarred quantities, which permits all of the calculations associated with the matching to be performed using real number arithmetic, a considerable computational simplification. Regarding the real coefficients appearing in these equations as elements of matrices, we can rewrite them as

$$\mathbf{h}_J^{\lambda+} \mathbf{C}_{j_\lambda}^{(i)+} + \mathbf{h}_J^{\lambda-} \mathbf{C}_{j_\lambda}^{(i)-} = \mathbf{s}_{\nu\lambda}^J \{ \mathbf{f}_J^{\nu+} \mathbf{C}_{j_\nu}^{(i)+} + \mathbf{f}_J^{\nu-} \mathbf{C}_{j_\nu}^{(i)-} \} \quad (4.32)$$

and

$$\mathbf{h}_J^{\lambda+} \mathbf{C}_{j_\lambda}^{(i)+} + \mathbf{h}_J^{\lambda-} \mathbf{C}_{j_\lambda}^{(i)-} = \mathbf{s}_{\nu\lambda}^J \{ \mathbf{f}_J^{\nu+} \mathbf{C}_{j_\nu}^{(i)+} + \mathbf{f}_J^{\nu-} \mathbf{C}_{j_\nu}^{(i)-} \}. \quad (4.33)$$

The matrix $\mathbf{s}_{\nu\lambda}^J$ is related to $\bar{s}_{\nu\lambda}^J$ by the unitary transformation $\bar{\mathbf{I}}^\dagger \mathbf{s}_{\nu\lambda}^J \bar{\mathbf{I}}$, where $\bar{\mathbf{I}}$ is the unitary diagonal matrix whose diagonal elements alternate between 1 and i . Therefore, if the $B^{\nu\lambda}$ form a complete set, $\mathbf{s}_{\nu\lambda}^J$ is unitary, and since it is real it is also orthogonal. As shown in the previous section, the number of basis functions $B_{\nu\lambda j_\lambda}^{\nu\lambda}$ used to expand the wavefunction on $\pi_{\nu\lambda}$ is $N/2$, where N is the total number of vibration-rotation functions used in the coupled-channel expansion. This implies that there should only be $N/2$ rows in the matrices $\mathbf{h}_J^{\lambda\pm}$. There are, however, N columns because the different columns denote the N linearly independent solutions propagated in either the forward (+) or backwards (-) integrations. Summarizing, the dimensions of the various matrices in Eqs. (4.32) or (4.33) are symbolically represented as follows:

$$(N/2 \times N)(N \times N) + (N/2 \times N)(N \times N) \\ = (N/2 \times N/2) [(N/2 \times N)(N \times N) + (N/2 \times N)(N \times N)] \quad (4.34)$$

We can combine Eqs. (4.32) and (4.33) into a single expression which contains only square $N \times N$ matrices by defining the augmented $N \times N$ matrices $\hat{\mathbf{h}}_J^{\lambda\pm}$, $\hat{\mathbf{f}}_J^{\nu\pm}$, and $\hat{\mathbf{s}}_{\nu\lambda}^J$ as

$$\hat{\mathbf{h}}_J^{\lambda\pm} = \begin{pmatrix} \mathbf{h}_J^{\lambda\pm} \\ \mathbf{h}'^{\lambda\pm} \end{pmatrix}, \quad (4.35)$$

$$\hat{\mathbf{f}}_J^{\nu\pm} = \begin{pmatrix} \mathbf{f}_J^{\nu\pm} \\ \mathbf{f}'^{\nu\pm} \end{pmatrix}, \quad (4.36)$$

$$\hat{\mathbf{s}}_{\nu\lambda}^J = \begin{pmatrix} \mathbf{s}_{\nu\lambda}^J & \mathbf{0} \\ \mathbf{0} & \mathbf{s}_{\nu\lambda}^J \end{pmatrix}, \quad (4.37)$$

where $\mathbf{0}$ denotes an $(N/2 \times N/2)$ matrix of zeros. The resulting matching equation on $\pi_{\nu\lambda}$ becomes

$$\hat{\mathbf{h}}_J^{\lambda+} \mathbf{C}_{J\lambda}^{(i)+} + \hat{\mathbf{h}}_J^{\lambda-} \mathbf{C}_{J\lambda}^{(i)-} = \hat{\mathbf{s}}_{\nu\lambda}^J (\hat{\mathbf{f}}_J^{\nu+} \mathbf{C}_{J\nu}^{(i)+} + \hat{\mathbf{f}}_J^{\nu-} \mathbf{C}_{J\nu}^{(i)-}) \quad (4.38)$$

In order to solve for the unknown coefficient matrices $\mathbf{C}_{J\lambda}^{(i)\pm}$, $\mathbf{C}_{J\nu}^{(i)\pm}$ (and $\mathbf{C}_{J\kappa}^{(i)\pm}$), we must couple Eq. (4.38) with the corresponding equations obtained from the matching on $\pi_{\kappa\nu}$ and $\pi_{\lambda\kappa}$. Using the same notation as in Eq. (4.38), the matching equations on these two additional surfaces are

$$\hat{\mathbf{h}}_J^{\nu+} \mathbf{C}_{J\nu}^{(i)+} + \hat{\mathbf{h}}_J^{\nu-} \mathbf{C}_{J\nu}^{(i)-} = \hat{\mathbf{s}}_{\kappa\nu}^J (\hat{\mathbf{f}}_J^{\kappa+} \mathbf{C}_{J\kappa}^{(i)+} + \hat{\mathbf{f}}_J^{\kappa-} \mathbf{C}_{J\kappa}^{(i)-}) \quad (4.39)$$

and

$$\hat{\mathbf{h}}_J^{\kappa+} \mathbf{C}_{J\kappa}^{(i)+} + \hat{\mathbf{h}}_J^{\kappa-} \mathbf{C}_{J\kappa}^{(i)-} = \hat{\mathbf{s}}_{\lambda\kappa}^J (\hat{\mathbf{f}}_J^{\lambda+} \mathbf{C}_{J\lambda}^{(i)+} + \hat{\mathbf{f}}_J^{\lambda-} \mathbf{C}_{J\lambda}^{(i)-}) \quad (4.40)$$

We can now combine Eqs. (4.38), (4.39), and (4.40) into the following single matrix equation which involves square matrices of dimension $3N \times 3N$:

$$\mathbf{N}_J^+ \mathbf{C}_J^+ + \mathbf{N}_J^- \mathbf{C}_J^- = \mathbf{0}, \quad (4.41)$$

where

$$\mathbf{N}_J^{\pm} = \begin{pmatrix} \hat{\mathbf{h}}_J^{\lambda\pm} & -\hat{\mathbf{s}}_{\nu\lambda}^J \hat{\mathbf{f}}_J^{\nu\pm} & \mathbf{0} \\ \mathbf{0} & \hat{\mathbf{h}}_J^{\nu\pm} & -\hat{\mathbf{s}}_{\kappa\nu}^J \hat{\mathbf{f}}_J^{\kappa\pm} \\ -\hat{\mathbf{s}}_{\lambda\kappa}^J \hat{\mathbf{f}}_J^{\lambda\pm} & \mathbf{0} & \hat{\mathbf{h}}_J^{\kappa\pm} \end{pmatrix}, \quad (4.42)$$

$$\mathbf{C}_J^{\pm} = \begin{pmatrix} \mathbf{C}_{J\lambda}^{(1)\pm} & \mathbf{C}_{J\lambda}^{(2)\pm} & \mathbf{C}_{J\lambda}^{(3)\pm} \\ \mathbf{C}_{J\nu}^{(1)\pm} & \mathbf{C}_{J\nu}^{(2)\pm} & \mathbf{C}_{J\nu}^{(3)\pm} \\ \mathbf{C}_{J\kappa}^{(1)\pm} & \mathbf{C}_{J\kappa}^{(2)\pm} & \mathbf{C}_{J\kappa}^{(3)\pm} \end{pmatrix}, \quad (4.43)$$

and the $\mathbf{0}$ stands for a matrix of zeros of the appropriate dimensionality. Let us rearrange Eq. (4.41) to the form

$$\mathbf{C}_J^+ (\mathbf{C}_J^-)^{-1} = -(\mathbf{N}_J^+)^{-1} \mathbf{N}_J^-. \quad (4.44)$$

Equation (4.44) is the essential result of the smooth matching procedure. It expresses the unknown coefficients \mathbf{C}_J^{\pm} in terms of the known \mathbf{N}_J^{\pm} and thus determines which linear combination of the solutions obtained from the integrations in each arrangement channel region will produce smoothly matched wavefunctions. Of course, Eq. (4.44) supplies only one $3N \times 3N$ matrix

equation for the two $3N \times 3N$ unknown matrices \mathbf{C}_J^{\pm} . This tells us that our matched solutions are not completely unique, which is not unexpected since we have not yet specified the asymptotic conditions which our matched wavefunctions must satisfy. We will do so in the next section, and when these additional conditions are combined with Eq. (4.44), we will obtain unique expressions for the coefficient matrices \mathbf{C}_J^{\pm} .

V. ASYMPTOTIC ANALYSIS

A. The reactance and scattering matrices

We will now describe how to obtain the reactance (\mathbf{R}_J) and scattering (\mathbf{S}_J) matrices from the asymptotic values of the primitive (but smoothly matched) solutions $\Psi_J^{(i)vf}$ described in the previous section. These functions are defined in the entire configuration space. Their asymptotic behavior in each of the three arrangement channels $\lambda = \alpha, \beta, \gamma$ can be obtained from Eqs. (3.22), (3.5), (2.13), (2.10), and (4.25) and is

$$\Psi_J^{(i)vf} \underset{R_\lambda \rightarrow \infty}{\sim} \varphi_J(\theta_\lambda) \sum_{\nu\lambda} \frac{\varphi_{J\lambda}(\gamma_\lambda) \phi_{\nu\lambda}^{\lambda}(r_\lambda)}{\sqrt{r_\lambda} R_\lambda} \\ \times \sum_{\nu', j'} \left(g_{J\nu\lambda}^{\lambda\nu' j' \lambda'} C_{J\nu\lambda}^{(i)vf+} + g_{J\nu\lambda}^{\lambda\nu' j' \lambda'} C_{J\nu\lambda}^{(i)vf-} \right) \\ \lambda = \alpha, \beta, \gamma, \quad (5.1)$$

where we have dropped the superscript (α) as it will be implicit throughout Sec. V. The product functions $r_\lambda^{-1/2} \varphi_{J\lambda}(\gamma_\lambda) \phi_{\nu\lambda}^{\lambda}(r_\lambda)$ are the asymptotic vibration-rotation wavefunctions of the diatomic molecule corresponding to the λ arrangement channel. We note that $\phi_{\nu\lambda}^{\lambda}(r_\lambda)$ vanishes in the asymptotic regions of arrangement channels ν and κ because $r_\lambda \rightarrow \infty$ in these regions. As a result, Eq. (5.1) can be rewritten as

$$\Psi_J^{(i)vf} \sim \sum_{\lambda} \varphi_J(\theta_\lambda) \sum_{\nu\lambda} \frac{\varphi_{J\lambda}(\gamma_\lambda) \phi_{\nu\lambda}^{\lambda}(r_\lambda)}{\sqrt{r_\lambda} R_\lambda} e_{J\nu\lambda}^{(i)vf}(R_\lambda), \quad (5.2)$$

where

$$e_{J\nu\lambda}^{(i)vf} = \sum_{\nu', j'} \left(g_{J\nu\lambda}^{\lambda\nu' j' \lambda'} C_{J\nu\lambda}^{(i)vf+} + g_{J\nu\lambda}^{\lambda\nu' j' \lambda'} C_{J\nu\lambda}^{(i)vf-} \right), \quad (5.3)$$

and the λ summation extends over arrangement channels α, β , and γ . The analogous expression for the function $R_\lambda^{-1/2} (\partial/\partial R_\lambda) (R_\lambda^{1/2} \Psi_J^{(i)vf})$ is obtained from Eqs. (5.2) and (5.3) by replacing $g_{J\nu\lambda}^{\lambda\nu' j' \lambda'}$ by $dg_{J\nu\lambda}^{\lambda\nu' j' \lambda'}/dR_\lambda$ in the latter.

We now define the reactance and scattering matrix solutions for each partial wave J . In analogy with their corresponding three-dimensional multichannel definitions,^{38,39} and using the asymptotic behavior of the coplanar solutions given in Eqs. (3.26), we define the reactance and scattering solutions and the corresponding matrices as follows:

$$\Psi_J^{\lambda' \nu' j'} [R \text{ or } S] \sim \sum_{\lambda} \varphi_J(\theta_\lambda) \\ \sum_{\nu\lambda} \frac{\varphi_{J\lambda}(\gamma_\lambda) \phi_{\nu\lambda}^{\lambda}(r_\lambda)}{\sqrt{r_\lambda} R_\lambda} b_{J\nu\lambda}^{\lambda' \nu' j'} [R \text{ or } S], \quad (5.4)$$

where, for the \mathbf{R}_J matrix solution,

$$b_{J\lambda v_{\lambda} j_{\lambda}}^{\lambda' v_{\lambda'} j_{\lambda'}}[R] = \left(\frac{\mu R_{\lambda}}{\hbar}\right)^{1/2} \begin{cases} I_{J-J_{\lambda}}(k_{v_{\lambda} j_{\lambda}}^{\lambda} R_{\lambda}) \delta_{\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}} + Y_{J-J_{\lambda}}(k_{v_{\lambda} j_{\lambda}}^{\lambda} R_{\lambda}) R_{J\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}}, & \text{(for the open channels)} \\ I_{J-J_{\lambda}}(|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda}) \delta_{\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}} + K_{J-J_{\lambda}}(|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda}) R_{J\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}}, & \text{(for the closed channels)}, \end{cases} \quad (5.5)$$

and for the \mathbf{S}_J matrix solution

$$b_{J\lambda v_{\lambda} j_{\lambda}}^{\lambda' v_{\lambda'} j_{\lambda'}}[S] = \left(\frac{\mu R_{\lambda}}{\hbar}\right)^{1/2} \begin{cases} H_{J-J_{\lambda}}^{(2)}(k_{v_{\lambda} j_{\lambda}}^{\lambda} R_{\lambda}) \delta_{\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}} + H_{J-J_{\lambda}}^{(1)}(k_{v_{\lambda} j_{\lambda}}^{\lambda} R_{\lambda}) S_{J\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}}, & \text{(for the open channels)} \\ I_{J-J_{\lambda}}(|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda}) \delta_{\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}} + K_{J-J_{\lambda}}(|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda}) S_{J\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}}, & \text{(for the closed channels)}, \end{cases} \quad (5.6)$$

and the Hankel functions H_i are related to the Bessel functions J_i , Y_i by

$$H_i^{(1,2)} = J_i \pm i Y_i. \quad (5.7)$$

The asymptotic sign in Eq. (5.4) signifies that for each λ in the summation the corresponding R_{λ} goes to infinity. The \mathbf{R}_J and \mathbf{S}_J matrices defined in Eqs. (5.5) and (5.6) have dimension $3N \times 3N$ and include both open and closed channel initial and final states. Only the open \rightarrow open transitions have direct physical significance, and we will label the submatrices formed by the corresponding matrix elements by the symbols \mathbf{R}_J^0 and \mathbf{S}_J^0 . It is these open channel matrices \mathbf{R}_J^0 and \mathbf{S}_J^0 which obey the usual properties that \mathbf{R}_J^0 is real and symmetric and \mathbf{S}_J^0 is unitary and symmetric,²⁴ as a result of the time reversal invariance and conservation of flux properties of the Schrödinger equation. Actually, Eqs. (5.4)–(5.7) are expressed in terms of the mass-scaled variables r_{λ} , R_{λ} of Eqs. (2.2a) and (2.2b), whereas the reactive and scattering matrices we are interested in are defined in terms of equivalent expressions involving the unscaled \bar{r}_{λ} , \bar{R}_{λ} . However, Eq. (5.4) and its unscaled variable counterpart are proportional to one another, and as a result \mathbf{R}_J and \mathbf{S}_J are invariant under the r_{λ} , $R_{\lambda} \rightarrow \bar{r}_{\lambda}$, \bar{R}_{λ} transformation; this permits us to use directly the unbarred variable results to calculate these matrices. From Eqs. (5.7), Eqs. (5.5) and (5.6), we can obtain the following relation between the open channel subblocks of the reactance and scattering matrices, analogous to the one valid for three dimensions^{38, 39}:

$$\mathbf{S}_J^0 = (\mathbf{I} - i\mathbf{R}_J^0)(\mathbf{I} + i\mathbf{R}_J^0)^{-1}, \quad (5.8)$$

where \mathbf{I} is the identity matrix. We will discuss the physical significance of the scattering matrix at the end of this section.

Let us indicate how \mathbf{R}_J can be obtained from the numerically determined solutions $\Psi_J^{(i) v j}$. We rewrite Eqs. (5.3) and (5.5) in $3N \times 3N$ matrix form as

$$\mathbf{e}_J = \mathbf{g}_J^+ \mathbf{C}_J^+ + \mathbf{g}_J^- \mathbf{C}_J^- \quad (5.9)$$

and

$$\mathbf{b}_J = \mathbf{V}^{-1/2} (\mathbf{J}_J + \mathbf{Y}_J \tilde{\mathbf{R}}_J), \quad (5.10)$$

where

$$(\mathbf{g}_J^{\pm})_{\lambda v_{\lambda} j_{\lambda}}^{\lambda' v_{\lambda'} j_{\lambda'}} = \delta_{\lambda \lambda'} g_{J\lambda' v_{\lambda'} j_{\lambda'}}^{\lambda v_{\lambda} j_{\lambda}}, \quad (5.11)$$

$$(\mathbf{V}^{-1/2})_{\lambda v_{\lambda} j_{\lambda}}^{\lambda' v_{\lambda'} j_{\lambda'}} = \delta_{\lambda \lambda'} \delta_{v_{\lambda} j_{\lambda}}^{v_{\lambda'} j_{\lambda'}} (V_{v_{\lambda} j_{\lambda}}^{\lambda})^{-1/2}, \quad (5.12a)$$

$$V_{v_{\lambda} j_{\lambda}}^{\lambda} = \hbar k_{v_{\lambda} j_{\lambda}}^{\lambda} / \mu, \quad (5.12b)$$

$$(\mathbf{J}_J)_{\lambda v_{\lambda} j_{\lambda}}^{\lambda' v_{\lambda'} j_{\lambda'}} = \delta_{\lambda \lambda'} \delta_{v_{\lambda} j_{\lambda}}^{v_{\lambda'} j_{\lambda'}} (|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda})^{1/2} \times \begin{cases} J_{J-J_{\lambda}}(k_{v_{\lambda} j_{\lambda}}^{\lambda} R_{\lambda}) & \text{(open channels)} \\ I_{J-J_{\lambda}}(|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda}) & \text{(closed channels)}, \end{cases} \quad (5.13)$$

$$(\mathbf{Y}_J)_{\lambda v_{\lambda} j_{\lambda}}^{\lambda' v_{\lambda'} j_{\lambda'}} = \delta_{\lambda \lambda'} \delta_{v_{\lambda} j_{\lambda}}^{v_{\lambda'} j_{\lambda'}} (|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda})^{1/2} \times \begin{cases} Y_{J-J_{\lambda}}(k_{v_{\lambda} j_{\lambda}}^{\lambda} R_{\lambda}) & \text{(open channels)} \\ K_{J-J_{\lambda}}(|k_{v_{\lambda} j_{\lambda}}^{\lambda}| R_{\lambda}) & \text{(closed channels)}, \end{cases} \quad (5.14)$$

and $\tilde{\mathbf{R}}_J$ is the transpose of \mathbf{R}_J . The elements of the \mathbf{e}_J and \mathbf{b}_J matrices are the $e_{J\lambda v_{\lambda} j_{\lambda}}^{(i) v j}$ and $b_{J\lambda v_{\lambda} j_{\lambda}}^{(i) v j}[R]$, respectively. In all these matrix elements, the subscripts other than J denote the row and the superscripts the column to which they belong. The reactance matrix solution $\Psi_J^{\lambda' v_{\lambda'} j_{\lambda'}}[R]$ can be obtained from our numerically determined solutions $\Psi_J^{(i) v j}$ by taking linear combinations of the latter:

$$\Psi_J^{\lambda' v_{\lambda'} j_{\lambda'}}[R] = \sum_{i=1}^3 \sum_{v j} \Psi_J^{(i) v j} Q_{(i) v j}^{\lambda' v_{\lambda'} j_{\lambda'}}. \quad (5.15)$$

As was mentioned at the end of Sec. IV, the matching equation [Eq. (4.44)] determines \mathbf{C}_J^+ (\mathbf{C}_J^-)⁻¹ but not \mathbf{C}_J^+ or \mathbf{C}_J^- individually. To complete their evaluation we choose $Q_{(i) v j}^{\lambda' v_{\lambda'} j_{\lambda'}} = \delta_{(i) v j}^{\lambda' v_{\lambda'} j_{\lambda'}}$ in Eq. (5.15), which is equivalent to requiring that the \mathbf{C}_J^+ produce solutions which are not only smoothly matched, but satisfy the reactance asymptotic conditions as well. (It will soon become apparent that there are enough degrees of freedom left over to permit this condition to be imposed.) We then substitute Eqs. (5.2) and (5.4) into Eq. (5.15) and equate coefficients of terms having the same arrangement channel λ and vibration-rotation basis functions $r_{\lambda}^{-1/2} \phi_{j_{\lambda}}(\gamma_{\lambda}) \phi_{v_{\lambda} j_{\lambda}}(r_{\lambda})$. Expressing the resulting equations in matrix form and using Eqs. (5.9) and (5.10), we obtain

$$(\mathbf{g}_J^+ \mathbf{C}_J^+ + \mathbf{g}_J^- \mathbf{C}_J^-) = \mathbf{V}^{-1/2} (\mathbf{J}_J + \mathbf{Y}_J \tilde{\mathbf{R}}_J). \quad (5.16)$$

The analogous equation for the derivative $(R_{\lambda})^{-1/2} (\partial / \partial R_{\lambda}) [(R_{\lambda})^{1/2} \Psi_J[R]]$ is

$$(\mathbf{g}_J' \mathbf{C}_J^+ + \mathbf{g}_J' \mathbf{C}_J^-) = \mathbf{V}^{-1/2} (\mathbf{J}_J' + \mathbf{Y}_J' \tilde{\mathbf{R}}_J), \quad (5.17)$$

where prime denotes differentiation with respect to R_{λ} , with $\lambda = \alpha, \beta, \gamma$ as appropriate. These last two equa-

tions and Eq. (4.44) can then be simultaneously solved to yield the following expression for $\bar{\mathbf{R}}_J$:

$$\bar{\mathbf{R}}_J = -\mathbf{V}^{1/2} \mathbf{W}_J^{-1} [(\mathbf{J}_J' \mathbf{g}_J^{*'}) (\mathbf{N}_J^*)^{-1} \mathbf{N}_J - (\mathbf{J}_J' \mathbf{g}_J - \mathbf{J}_J \mathbf{g}_J^{*'})] \\ \times [(\mathbf{Y}_J' \mathbf{g}_J^{*'} - \mathbf{Y}_J \mathbf{g}_J^{*'}) (\mathbf{N}_J^*)^{-1} \mathbf{N}_J - (\mathbf{Y}_J' \mathbf{g}_J - \mathbf{Y}_J \mathbf{g}_J^{*'})]^{-1} \mathbf{W}_J \mathbf{V}^{-1/2} \quad (5.18)$$

where

$$\mathbf{W}_J = \mathbf{Y}_J' \mathbf{J}_J - \mathbf{J}_J' \mathbf{Y}_J \quad (5.19)$$

is the diagonal matrix whose diagonal elements are the Wronskians of the regular and irregular ordinary or modified Bessel functions.³³ None of the matrices whose inverses appear in Eq. (5.18) are in general singular. Transposition of Eq. (5.18) gives \mathbf{R}_J , and Eqs. (5.18) and (4.44) when substituted into Eqs. (5.16) or (5.17) permit an explicit and unique determination of \mathbf{C}_J^+ and \mathbf{C}_J^- .

The procedure just described furnished the full \mathbf{R}_J matrix. Its closed channel parts may now be discarded and the open channel part of the scattering matrix \mathbf{S}_J^0 may then be used to calculate $P_{J\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}$, the probability of transition from a given initial arrangement channel λ' and internal state v_λ, j_λ (for a given total angular momentum quantum number J) through the relation

$$P_{J\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'} = |S_{J\lambda v_\lambda j_\lambda}^{0\lambda' v_\lambda' j_\lambda'}|^2. \quad (5.20)$$

Note that this is a distinguishable-atom transition probability. Effects of indistinguishability of particles will

be considered in Sec. VI, B. As mentioned in Sec. II, C, the total angular momentum is simply equal to the algebraic sum of the rotational and orbital angular momenta, i.e., $J = j_\lambda + l_\lambda$, which allows us to re-express $P_{J\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}$ in terms of initial and final orbital angular momenta l_λ and l_λ' . This has a useful semiclassical interpretation since the initial orbital angular momentum quantum number l_λ is related to the classical impact parameter b_λ through the relation

$$l_\lambda = \bar{k}_{v_\lambda j_\lambda}^\lambda b_\lambda, \quad (5.21)$$

where $\bar{k}_{v_\lambda j_\lambda}^\lambda$ is the wave number in the $\bar{R}_\lambda, \bar{r}_\lambda$ coordinate system (defined in Sec. II, B)

$$\bar{k}_{v_\lambda j_\lambda}^\lambda = \left(\frac{2\mu_{\lambda v_\lambda}}{\hbar^2} (E - \epsilon_{v_\lambda j_\lambda}^\lambda) \right)^{1/2} \\ = \alpha_\lambda k_{v_\lambda j_\lambda}^\lambda. \quad (5.22)$$

B. Distinguishable-atom scattering amplitudes and cross sections

In this section we define a coplanar dimensionless distinguishable-atom scattering amplitude and give its relation to the coplanar scattering matrix and differential and integral cross sections.

Let $\Psi^{\lambda v_\lambda j_\lambda}[P]$ be a "physical" solution to the Schrödinger equation (2.4), involving the mass-scaled coordinates $\mathbf{r}_\lambda, R_\lambda$, which behaves asymptotically at large R_λ, R_ν , and R_κ as

$$\Psi^{\lambda v_\lambda j_\lambda}[P] \sim \sum_{\lambda' v_\lambda' j_\lambda'} \left[\delta_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'} e^{ik_{v_\lambda j_\lambda}^\lambda R_\lambda} \cos \theta_\lambda + \left(\frac{\hbar}{\mu |V_{\lambda v_\lambda j_\lambda}^\lambda|} \right)^{1/2} \hat{f}_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}(\theta_\lambda) R_\lambda^{-1/2} e^{ik_{v_\lambda j_\lambda}^{\lambda'} R_\lambda} \right] \varphi_{j_\lambda}(\theta_{r_\lambda}) r_\lambda^{-1/2} \phi_{v_\lambda j_\lambda}^{\lambda'}(r_\lambda). \quad (5.23)$$

This solution describes a collision between atom A_λ and molecule $A_\nu A_\kappa$ in internal vibrational-rotational state $v_\lambda j_\lambda$, with the relative initial velocity of colliding partners, in scaled coordinates, being $V_{v_\lambda j_\lambda}^\lambda$. The direction of relative approach of the colliding partners is the x axis of Fig. 1. The scaled coordinate relative motion wave number $k_{v_\lambda j_\lambda}^\lambda$ is real positive for open channels and imaginary positive for closed ones. The first and second R_λ -dependent terms in Eq. (5.23) represent, respectively, the incident relative motion line wave and the scattered circular wave, which can be nonreactive ($\lambda' = \lambda$) or reactive ($\lambda' \neq \lambda$). These are the 2D analogues of the 3D incident plane wave and scattered spherical waves. The factor outside the square brackets is the planar-motion vibrational-rotational wavefunction of the isolated A_ν, A_κ molecule in state v_λ, j_λ , in scaled coordinates.

Equation (5.23) defines a set of dimensionless distinguishable atom scattering amplitudes $\hat{f}(\theta_\lambda)$. The differential cross section for the $\lambda v_\lambda j_\lambda \rightarrow \lambda' v_\lambda' j_\lambda'$ process (assuming that both these states are open at the total energy E being considered) is related to the corresponding \hat{f} by

$$\sigma_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}(\theta_\lambda) = (1/\bar{k}_{v_\lambda j_\lambda}^\lambda) |\hat{f}_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}|^2, \quad (5.24)$$

where $\bar{k}_{v_\lambda j_\lambda}^\lambda$ is the unscaled initial relative motion wave number of the colliding particles. For either reactive or nonreactive collisions, θ_λ is the angle between the initial and final velocity vectors of the atom with respect to the diatom in the center of mass system Oxy of Fig. 1. The integral cross section for the same process is

$$Q_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'} = \int_0^{2\pi} \sigma_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}(\theta_\lambda) d\theta_\lambda. \quad (5.25)$$

σ and Q have dimensions of a length per unit angle and of a length, respectively.

We now relate the scattering amplitudes to the scattering matrix. To do this, we expand the physical solution Eq. (5.23) in terms of the scattering matrix solution [Eqs. (5.4) and (5.6)] using an equation analogous to (2.12):

$$\Psi^{\lambda v_\lambda j_\lambda}[P] = \sum_{j=-\infty}^{\infty} C_J^{\lambda v_\lambda j_\lambda} \Psi_J^{\lambda v_\lambda j_\lambda}[S]. \quad (5.26)$$

To find expressions for the coefficients $C_J^{\lambda v_\lambda j_\lambda}$ and the scattering amplitudes $\hat{f}_{\lambda v_\lambda j_\lambda}^{\lambda' v_\lambda' j_\lambda'}$, we first expand the θ_λ -dependent portions of Eq. (5.23) in terms of the eigenfunctions $\varphi_J(\theta_\lambda)$, then express the R_λ -dependent portions of Eqs. (5.23) and (5.6) in their asymptotic forms

[Eq. (3.27)] involving exponentials. We finally equate the coefficients of the corresponding R_{λ} exponentials, $\varphi_J(\theta_{\lambda})$ and rotation-vibration basis functions in both sides of Eq. (5.26) and solve the resulting equations for $C_{J\lambda\nu\lambda}^{\lambda'}$ and for the coefficients of the expansion of $\hat{f}_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}}(\theta_{\lambda'})$ in the $\varphi_J(\theta_{\lambda'})$.

The expansion for the line wave is⁴⁰

$$e^{ik_{\lambda}^{\lambda'}j_{\lambda'}R_{\lambda'}\cos\theta_{\lambda'}} = \sum_{J=-\infty}^{\infty} i^J e^{iJ\theta_{\lambda'}} J_J(k_{\lambda}^{\lambda'}j_{\lambda'}R_{\lambda'}) ,$$

$$R_{\lambda'} \sim \frac{1}{k_{\lambda}^{\lambda'}j_{\lambda'}R_{\lambda'}} \sum_{J=-\infty}^{\infty} \left[e^{ik_{\lambda}^{\lambda'}j_{\lambda'}R_{\lambda'}} e^{-i(\pi/4)} + (-1)^J e^{-ik_{\lambda}^{\lambda'}j_{\lambda'}R_{\lambda'}} e^{i(\pi/4)} \right] \varphi_J(\theta_{\lambda'}) \quad (5.27)$$

As a result of the relation between γ_{λ} , θ_{λ} , and $\theta_{r_{\lambda}}$ given after Eq. (2.1), and of Eq. (2.9), we have

$$\varphi_{j_{\lambda}}(\theta_{r_{\lambda}}) = (2\pi)^{1/2} \varphi_{j_{\lambda}}(\theta_{\lambda}) \varphi_{j_{\lambda}}(\gamma_{\lambda}) . \quad (5.28)$$

Using Eqs. (5.26)–(5.28) and following the procedure outlined above, we get

$$C_{J\lambda\nu\lambda}^{\lambda'} = \left(\frac{\hbar\pi}{2\mu} \right)^{1/2} \exp[i(J-j_{\lambda})\frac{1}{2}\pi] \quad (5.29)$$

and, for the dimensionless scattering amplitudes to open channels,

$$\hat{f}_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}}(\theta_{\lambda'}) = \exp(-ij_{\lambda}\theta_{\lambda'}) \exp[i(j_{\lambda'} - j_{\lambda} - \frac{1}{2})\pi] \\ \times \sum_{J=-\infty}^{\infty} (S_{J\lambda\nu\lambda}^{0\lambda'v_{\lambda'}j_{\lambda'}} - \delta_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}}) \varphi_J(\theta_{\lambda'}) . \quad (5.30)$$

Equation (5.30) differs from that obtained by Walker and Wyatt⁴¹ only by the phase factor $\exp(-ij_{\lambda}\theta_{\lambda'})$. Substitution of Eq. (5.30) into (5.24) and of the result into Eq. (5.25) leads to the following rather simple expression for the integral cross section:

$$Q_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}} = \frac{1}{k_{\lambda}^{\lambda'}j_{\lambda'}} \sum_{J=-\infty}^{\infty} |S_{J\lambda\nu\lambda}^{0\lambda'v_{\lambda'}j_{\lambda'}} - \delta_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}}|^2 . \quad (5.31)$$

Equations (5.35) and (5.36) may be written in terms of a sum over J from 0 to ∞ by using the relation

$$S_{J\lambda\nu\lambda}^{0\lambda'v_{\lambda'}j_{\lambda'}} = S_{-J\lambda\nu\lambda}^{0\lambda'v_{\lambda'}-j_{\lambda'}} . \quad (5.32)$$

This expression is a consequence of the symmetry of the Hamiltonian with respect to reflection through the plane of motion. Additional symmetry relations which follow from Eq. (5.32) are

$$\hat{f}_{\lambda\nu\lambda-j_{\lambda}}^{\lambda'v_{\lambda'}-j_{\lambda'}}(2\pi - \theta_{\lambda'}) = \hat{f}_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}}(\theta_{\lambda'}) \quad (5.33)$$

and

$$Q_{\lambda\nu\lambda-j_{\lambda}}^{\lambda'v_{\lambda'}-j_{\lambda'}} = Q_{\lambda\nu\lambda}^{\lambda'v_{\lambda'}j_{\lambda'}} . \quad (5.34)$$

Equations (5.32), through (5.34) are valid for any planar atom plus diatomic molecule collision process. For reactions of higher symmetry such as $H+H_2$, there exist additional relationships, some of which will be discussed in the next section.

VI. APPLICATION TO PLANAR $H+H_2$

A. The integration, matching, and distinguishable-atom asymptotic analysis

In the application of the methods described in Sec. III and IV to the $H+H_2$ exchange reaction, a considerable reduction in computation time can be realized by utilizing two important symmetry properties of this collision system. The first is the invariance of the collision system and associated coordinate systems with respect to a cyclic permutation of the three atoms. Mathematically this means that all equations derived in Secs. III–V are invariant to a cyclic permutation of the indices $\lambda\nu\kappa$, which implies (1) that we need to integrate the Schrödinger equation in only one of the three arrangement channel regions depicted in Fig. 2, (2) that we need only calculate the projection coefficients \bar{h} , \bar{h}' , \bar{f} , and \bar{f}' defined in Eqs. (4.11), (4.12), (4.22), and (4.23) on one of the three matching surfaces (such as $\pi_{\nu\lambda}$), and (3) that the $\lambda \rightarrow \nu$, $\nu \rightarrow \kappa$, and $\kappa \rightarrow \lambda$ distinguishable-atom scattering amplitudes are all identical, as are $\nu \rightarrow \lambda$, $\lambda \rightarrow \kappa$, $\kappa \rightarrow \nu$, and $\lambda \rightarrow \lambda$, $\nu \rightarrow \nu$, $\kappa \rightarrow \kappa$, so we may restrict ourselves to a calculation of the $\lambda \rightarrow \lambda$, $\lambda \rightarrow \nu$, and $\lambda \rightarrow \kappa$ scattering amplitudes only. The second symmetry property is related to the invariance of the collision system (but *not* the associated coordinate systems) with respect to an interchange of any two of the three atoms. This results in a potential function $V^{\lambda}(r_{\lambda}, R_{\lambda}, \gamma_{\lambda})$ which is symmetric about $\gamma_{\lambda} = \pi/2$ and $3\pi/2$:

$$V^{\lambda}(r_{\lambda}, R_{\lambda}, \pi - \gamma_{\lambda}) = V^{\lambda}(r_{\lambda}, R_{\lambda}, \gamma_{\lambda}) \quad \text{for } 0 \leq \gamma_{\lambda} \leq \pi , \quad (6.1)$$

$$V^{\lambda}(r_{\lambda}, R_{\lambda}, 3\pi - \gamma_{\lambda}) = V^{\lambda}(r_{\lambda}, R_{\lambda}, \gamma_{\lambda}) \quad \text{for } \pi < \gamma_{\lambda} < 2\pi .$$

To a large extent, the consequences of this property depend on the coordinate system being used, for while Eq. (6.1) is valid in all regions of configuration space, the λ arrangement channel coordinates r_{λ} , R_{λ} , γ_{λ} are not the most convenient coordinates to use in all three arrangement channel regions. In arrangement channel region λ , Eq. (6.1) has the immediate effect of decoupling rotational states of even and odd quantum numbers j_{λ} . This means that the integration in arrangement channel region λ can be done in two separate steps, one for even j_{λ} and one for odd j_{λ} . In each of these steps the total number of basis functions required is only about half of that needed in the absence of this decoupling. Since the computation time varies as N^a , where N is the number of states being integrated and a is 2 for $N < 10$ and 3 for $N > 20$,²⁰ we see that a saving of factors of 2 to 4 in computation time may be realized by this decoupling. In a similar manner, the calculation of the matching surface coefficients of Eqs. (4.11), (4.12), (4.22), and (4.23) may be done in two separate steps, one for even j_{λ} and one for odd j_{λ} , and the coefficient matrices $f_{J'}^{\nu\pm}$ and $f_{J'}^{\nu*}$ may be obtained from $h_{J'}^{\lambda\pm}$ and $h_{J'}^{\lambda*}$ by using the simple relations

$$(f_{J'}^{\nu\pm})_{\nu\lambda j_{\lambda}}^{\nu'j_{\lambda}'} = (-1)^{j_{\lambda}+j_{\lambda}'} (h_{J'}^{\lambda\pm})_{\nu\lambda j_{\lambda}}^{\nu'j_{\lambda}'} , \quad (6.2a)$$

$$(f_{J'}^{\nu*})_{\nu\lambda j_{\lambda}}^{\nu'j_{\lambda}'} = -(-1)^{j_{\lambda}+j_{\lambda}'} (h_{J'}^{\lambda*})_{\nu\lambda j_{\lambda}}^{\nu'j_{\lambda}'} . \quad (6.2b)$$

We must note, however, that the number of matching surface functions $B_{\nu\lambda}^{\nu\lambda}$ is still $N/2$, where N is the total

number of even plus odd j_λ states. The matching procedure ultimately couples the even and odd rotational states j_λ [through Eq. (4.44)] so that decoupling beyond that point is lost. However, symmetry of the system about $\gamma_\lambda = \pi/2$ and $3\pi/2$ [Eq. (6.1)] may be used to relate the $\lambda \rightarrow \nu$ and $\lambda \rightarrow \kappa$ scattering amplitudes according to

$$\hat{f}_{\lambda\nu j}^{\nu\nu'j'} = (-1)^{j+j'} \hat{f}_{\lambda\nu j}^{\kappa\nu'j'}, \quad (6.3)$$

as is shown in Appendix C. Equation (6.3) may be used to reduce the work involved in the asymptotic analysis to the calculation of only the $\lambda \rightarrow \lambda$ and $\lambda \rightarrow \nu$ scattering amplitudes. An additional consequence of Eq. (6.1) valid only for the $\lambda \rightarrow \lambda$ scattering amplitudes (i.e., the nonreactive transitions) is the familiar relation (also derived in Appendix C)

$$\hat{f}_{\lambda\nu j}^{\lambda\nu'j'} = 0 \quad \text{for } j - j' = \text{odd}, \quad (6.4)$$

and the incorporation of this relation into the asymptotic analysis can also result in a reduction of computational effort. We should note, however, that the two symmetries given by Eqs. (6.3) and (6.4) depend on our use of a complete basis set $B_{\nu_\lambda j_\lambda}^\lambda$ for expanding the wavefunction on the matching surface and therefore may be used as a test of the convergence of the method provided these symmetries are not built into the calculations.

B. Postantisymmetrization

Up to this point, we have considered the three atoms to be distinguishable. However, to calculate physically measurable quantities such as cross sections for reactions like $\text{H} + \text{H}_2$, we must include for effects due to indistinguishability of the three atoms and the Pauli principle. This means that the physically meaningful solutions to the Schrödinger equation must be antisymmetric with respect to interchange of hydrogen nuclei (which have spin $\frac{1}{2}$). Some conceptual difficulties are occasionally encountered when using time-independent solutions, since antisymmetrization seems to imply incoming waves in all three arrangement channels asymptotically. A consideration of the time-dependent wavepacket generated from the time-independent solutions resolves this, however. As Taylor has shown,⁴² the asymptotic indistinguishable-atom wave packet is identical to its distinguishable-atom counterpart, so that at any given time before the collision, the incoming wave is localized in a single distinguishable-atom arrangement channel. Once the collision begins, such localization is lost and the concept of distinguishable-atom arrangement channels becomes meaningless.

There is actually a number of ways by which indistinguishable-atom scattering amplitudes may be obtained from time-independent wavefunctions:

1. We can preantisymmetrize the wavefunction, and solve the coupled integrodifferential equations generated when this wavefunction is substituted into the Schrödinger equation. Such a procedure was used by Wolken and Karplus¹⁶ and the resulting solutions yield directly the indistinguishable-atom scattering amplitudes.

2. We can solve the Schrödinger equation using the

method outlined in this paper for distinguishable particles, antisymmetrize the resultant primitive wavefunctions, and use the asymptotic form of these antisymmetrized wavefunctions to obtain the indistinguishable-atom scattering amplitudes. A related procedure was considered by Truhlar and Abdallah⁴³ in their method for studying rearrangement collisions.

3. We may use the distinguishable-atom primitive wavefunctions generated in (2) to determine the distinguishable-atom scattering amplitudes. These amplitudes may then be linearly combined to yield the corresponding indistinguishable-atom amplitudes. This is the usual procedure of postantisymmetrization²³ which we have used and which is described for the case of hydrogen atom exchange in Appendix D.

If exact solutions to the Schrödinger equation are used, then all three methods should give the same results, but the use of approximate solutions can lead to different results even when comparing methods (2) and (3) where the same distinguishable-atom primitive wavefunctions are used. An example of this arises when distinguishable-atom solutions that do not obey microscopic reversibility are considered. In this case the process of antisymmetrization of the wavefunction is not interchangeable with that of extracting the asymptotic form of the wavefunction, thus leading to different results when methods (2) and (3) are applied. Since the numerical method described in this paper is designed to provide accurate solutions to the Schrödinger equation for distinguishable atoms, the differences between methods (2) and (3) are of secondary importance and we shall restrict ourselves to considering method (3) for the remainder of this paper. The resulting expressions for the indistinguishable-particle transition amplitudes in terms of their distinguishable-atom counterparts, as described in Appendix D and also by Doll, George, and Miller,⁴⁴ are summarized below (where the direct and exchange amplitudes \hat{f}_1^λ and \hat{f}_2^λ of that Appendix are relabeled as \hat{f}_λ^λ and \hat{f}_ν^λ , respectively):

(a) para \rightarrow para:

$$\sigma_{\nu\nu'j'j}^{\nu\nu'j'}(\theta) = \frac{1}{k_\lambda^2} \left| \hat{f}_{\lambda\nu j}^{\lambda\nu'j'}(\theta) - \hat{f}_{\lambda\nu j}^{\nu\nu'j'}(\theta) \right|^2, \quad (6.5a)$$

(b) para \rightarrow ortho:

$$\sigma_{\nu\nu'j'j}^{\text{ortho}}(\theta) = \frac{3}{k_\lambda^2} \left| \hat{f}_{\lambda\nu j}^{\nu\nu'j'}(\theta) \right|^2, \quad (6.5b)$$

(c) ortho \rightarrow para:

$$\sigma_{\nu\nu'j'j}^{\text{para}}(\theta) = \frac{1}{k_\lambda^2} \left| \hat{f}_{\lambda\nu j}^{\nu\nu'j'}(\theta) \right|^2, \quad (6.5c)$$

(d) ortho \rightarrow ortho:

$$\sigma_{\nu\nu'j'j}^{\text{ortho}}(\theta) = \frac{1}{k_\lambda^2} \left[\left| \hat{f}_{\lambda\nu j}^{\lambda\nu'j'}(\theta) + \hat{f}_{\lambda\nu j}^{\nu\nu'j'}(\theta) \right|^2 + 2 \left| \hat{f}_{\lambda\nu j}^{\nu\nu'j'}(\theta) \right|^2 \right]. \quad (6.5d)$$

Note that there is no reference to arrangement channel on the left sides of Eqs. (6.5) since this distinction has no meaning after the effect of the Pauli principle is

included. The corresponding integral cross sections are

(a) para → para:

$$Q_{pvj}^{pp'} = \frac{1}{k_{vj}^\lambda} \sum_{j=-\infty}^{\infty} |S_{j\lambda vj}^{0\lambda v'j'} - \delta_{vj}^{v'j'} - S_{j\lambda vj}^{0\lambda v'j'}|^2, \quad (6.6a)$$

(b) para → ortho:

$$Q_{pvj}^{op'} = \frac{3}{k_{vj}^\lambda} \sum_{j=-\infty}^{\infty} |S_{j\lambda vj}^{0\lambda v'j'}|^2, \quad (6.6b)$$

(c) ortho → para:

$$Q_{ovj}^{pp'} = \frac{1}{k_{vj}^\lambda} \sum_{j=-\infty}^{\infty} |S_{j\lambda vj}^{0\lambda v'j'}|^2, \quad (6.6c)$$

(d) ortho → ortho:

$$Q_{ovj}^{op'} = \frac{1}{k_{vj}^\lambda} \sum_{j=-\infty}^{\infty} (|S_{j\lambda vj}^{0\lambda v'j'} - \delta_{vj}^{v'j'} + S_{j\lambda vj}^{0\lambda v'j'}|^2 + 2|S_{j\lambda vj}^{0\lambda v'j'}|^2). \quad (6.6d)$$

As expected, the para → ortho and ortho → para cross sections are simply proportional to the distinguishable-atom reactive cross sections since only exchange scattering amplitudes contribute to them. These cross sections furnish direct information on the reactive process alone. The para → para and ortho → ortho cross sections will show effects due to the interference between the reactive and nonreactive (i.e., direct and exchange) scattering amplitudes. The interference effects should be most important when these two amplitudes have comparable magnitudes. We will discuss this interference phenomenon in more detail when presenting our results for planar $H+H_2$.²⁰ As pointed out in Appendix D, Eqs. (6.5) above are also valid for the three-dimensional $H+H_2$ reaction once the quantum numbers m_j are added to the v and j ones and k_{vj}^λ is replaced by $(k_{vj}^\lambda)^2$.

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APPENDIX A: THE $\lambda \rightarrow \nu$ TRANSFORMATION EQUATIONS AND RELATIONS ON THE MATCHING SURFACES

In this Appendix we derive the important relations between the mass-scaled coordinates R_λ, r_λ ($\lambda = \alpha, \beta, \gamma$) defined by Eqs. (2.2). They permit us to change from coordinates appropriate for one arrangement channel to those appropriate for another one. We also examine the simplifications that occur when these relationships are evaluated on the matching surfaces defined by Eq. (3.2). This will allow us to prove that these surfaces are half-planes whose edge is the OY_λ axis in the $OX_\lambda Y_\lambda Z_\lambda$ space introduced in Sec. III. A. We will consider only the relationships between the arrangement

channel coordinates R_λ, r_λ and R_ν, r_ν explicitly. The corresponding relationships between R_ν, r_ν and R_κ, r_κ , and between R_κ, r_κ and R_λ, r_λ may be obtained by cyclic permutation of the indices $\lambda\nu\kappa$.

The following relations between the vectors $\bar{R}_\lambda, \bar{F}_\lambda$ and \bar{R}_ν, \bar{F}_ν , valid for any configuration of the three atoms, follows from Fig. 1:

$$\bar{R}_\nu = -\bar{F}_\lambda - \frac{m_\lambda}{m_\lambda + m_\kappa} \bar{F}_\nu$$

$$\bar{F}_\nu = \bar{R}_\lambda - \frac{m_\nu}{m_\nu + m_\kappa} \bar{F}_\lambda.$$

From these and Eqs. (2.2) we get

$$\begin{pmatrix} R_\nu \\ r_\nu \end{pmatrix} = \mathbf{M} \begin{pmatrix} R_\lambda \\ r_\lambda \end{pmatrix}, \quad (A1)$$

where \mathbf{M} is the 2×2 orthogonal matrix

$$\mathbf{M} = \begin{pmatrix} \cos \alpha_{\nu\lambda} & -\sin \alpha_{\nu\lambda} \\ \sin \alpha_{\nu\lambda} & \cos \alpha_{\nu\lambda} \end{pmatrix}, \quad (A2)$$

$\alpha_{\nu\lambda}$ being the angle between $\pi/2$ and π determined by

$$\cos \alpha_{\nu\lambda} = -\left(\frac{m_\lambda m_\nu}{(m_\lambda + m_\kappa)(m_\nu + m_\kappa)} \right)^{1/2} \quad (A3a)$$

and

$$\sin \alpha_{\nu\lambda} = \left(\frac{m_\kappa M}{(m_\lambda + m_\kappa)(m_\nu + m_\kappa)} \right)^{1/2}. \quad (A3b)$$

From these expressions we can get the equations for the $\theta_\lambda, R_\lambda, r_\lambda, \gamma_\lambda \rightarrow \theta_\nu, R_\nu, r_\nu, \gamma_\nu$ transformation. Indeed, from Eqs. (A1) and (A2) and the definition of γ_λ following Eq. (2.1) we get

$$R_\nu^2 = R_\nu \cdot R_\nu = \cos^2 \alpha_{\nu\lambda} R_\lambda^2 + \sin^2 \alpha_{\nu\lambda} r_\lambda^2 - \sin 2\alpha_{\nu\lambda} r_\lambda R_\lambda \cos \gamma_\lambda, \quad (A4)$$

$$r_\nu^2 = r_\nu \cdot r_\nu = \sin^2 \alpha_{\nu\lambda} R_\lambda^2 + \cos^2 \alpha_{\nu\lambda} r_\lambda^2 + \sin 2\alpha_{\nu\lambda} r_\lambda R_\lambda \cos \gamma_\lambda, \quad (A5)$$

and therefore

$$R_\nu^2 + r_\nu^2 = R_\lambda^2 + r_\lambda^2, \quad (A6)$$

which is a manifestation of the orthogonality of \mathbf{M} . In addition, it follows from Eqs. (A1) and (A2) that the cross products $\mathbf{R}_\lambda \times \mathbf{r}_\lambda$ and $\mathbf{R}_\nu \times \mathbf{r}_\nu$ are equal and therefore that

$$R_\nu r_\nu \sin \gamma_\nu = R_\lambda r_\lambda \sin \gamma_\lambda. \quad (A7a)$$

Since γ_ν is in the range $0-2\pi$, in order to have it completely specified we should obtain its cosine. Also from Eqs. (A4) and (A5) we get

$$\begin{aligned} \cos \gamma_\nu &= \frac{\mathbf{R}_\nu \cdot \mathbf{r}_\nu}{R_\nu r_\nu} \\ &= \frac{1}{R_\nu r_\nu} \left[\frac{1}{2} \sin 2\alpha_{\nu\lambda} (R_\lambda^2 - r_\lambda^2) + \cos 2\alpha_{\nu\lambda} \cos \gamma_\lambda R_\lambda r_\lambda \right]. \end{aligned} \quad (A7b)$$

Equations (A4), (A5), and (A7) completely describe the $R_\lambda, r_\lambda, \gamma_\lambda \rightarrow R_\nu, r_\nu, \gamma_\nu$ transformation. To complete the $\lambda \rightarrow \nu$ transformation we define the angle $\Delta_{\nu\lambda}$,

$$\Delta_{\nu\lambda} = \theta_\nu - \theta_\lambda, \quad (A8)$$

and express it in terms of the λ coordinates. We can write

$$\mathbf{R}_\lambda = R_\lambda (\cos\theta_\lambda \hat{\mathbf{x}} + \sin\theta_\lambda \hat{\mathbf{y}}),$$

$$\mathbf{r}_\lambda = r_\lambda [\cos(\theta_\lambda + \gamma_\lambda) \hat{\mathbf{x}} + \sin(\theta_\lambda + \gamma_\lambda) \hat{\mathbf{y}}],$$

where $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are the unit vectors along the laboratory-fixed axis depicted in Fig. 1. From these expressions, their ν counterpart and Eqs. (A1) and (A2) we can easily obtain the following expressions which determine $\Delta_{\nu\lambda}$ modulo 2π :

$$R_\nu \cos\Delta_{\nu\lambda} = R_\lambda \cos\alpha_{\nu\lambda} - r_\lambda \sin\alpha_{\nu\lambda} \cos\gamma_\lambda, \quad (\text{A9a})$$

$$R_\nu \sin\Delta_{\nu\lambda} = -r_\lambda \sin\alpha_{\nu\lambda} \sin\gamma_\lambda. \quad (\text{A9b})$$

We see that $\Delta_{\nu\lambda}$ is independent of θ_λ and a function of R_λ , r_λ , and γ_λ only. This is due to the fact that these three variables uniquely determine the internal configuration of the triatomic system and hence the angle $\Delta_{\nu\lambda}$ between \mathbf{R}_ν and \mathbf{R}_λ (see Fig. 1).

Equations (A4), (A5), and (A7)–(A9) completely describe the $\lambda \rightarrow \nu$ transformation. It is useful to obtain the expressions they reduce to on the $\pi_{\nu\lambda}$ surface defined by Eq. (3.2a). In view of this definition and of Eq. (A6) we have, on this surface,

$$r_\nu = r_\lambda, \quad (\text{A10a})$$

$$R_\nu = R_\lambda. \quad (\text{A10b})$$

From these and Eq. (A4) we get the very useful relation

$$R_\lambda/r_\lambda = -\cot\alpha_{\nu\lambda} \cos\gamma_\lambda + (1 + \cot^2\alpha_{\nu\lambda} \cos^2\gamma_\lambda)^{1/2} \quad (\text{A11})$$

between R_λ/r_λ and γ_λ on this surface. Other important relations among the internal variables are obtained by substituting Eqs. (A10) and (A11) into (A7). We find

$$\sin\gamma_\nu = \sin\gamma_\lambda$$

and, after some algebraic effort,

$$\cos\gamma_\nu = -\cos\gamma_\lambda,$$

which imply that

$$\gamma_\nu = \pi - \gamma_\lambda \pmod{2\pi}. \quad (\text{A12})$$

Since $0 \leq \gamma_\lambda \leq \pi/2$ or $3\pi/2 \leq \gamma_\lambda < 2\pi$, we see that $\pi/2 \leq \gamma_\nu \leq 3\pi/2$ on $\pi_{\nu\lambda}$.

From Eqs. (A10)–(A12) plus the expressions resulting from replacing those equations in (A9), the $\lambda \rightarrow \nu$ transformation equations on the $\pi_{\nu\lambda}$ matching surface are completely specified. In addition, since from Eqs. (A9) and (A10)

$$\cos\Delta_{\nu\lambda} = \cos\alpha_{\nu\lambda} - \sin\alpha_{\nu\lambda} \cos\gamma_\lambda (r_\lambda/R_\lambda) \quad (\text{A13a})$$

and

$$\sin\Delta_{\nu\lambda} = -(r_\lambda/R_\lambda) \sin\alpha_{\nu\lambda} \sin\gamma_\lambda, \quad (\text{A13b})$$

and since from Eq. (A11), r_λ/R_λ is a function of γ_λ only (on $\pi_{\nu\lambda}$), so is $\Delta_{\nu\lambda}$.

We shall now show that Eq. (A11) when evaluated over the range $0 \leq \gamma_\lambda \leq \pi/2$ and $3\pi/2 \leq \gamma_\lambda < 2\pi$ represents a half-plane whose edge is the OY_λ axis in the $OX_\lambda Y_\lambda Z_\lambda$ space defined in Sec. III. A and illustrated in Fig. 2. From Eqs. (3.1) and (A11), we obtain the simple expression

$$\cot\omega_\lambda = -\cot\alpha_{\nu\lambda} \cos\gamma_\lambda \quad 0 \leq \gamma_\lambda \leq \pi/2 \text{ and } 3\pi/2 \leq \gamma_\lambda < 2\pi \quad (\text{A14})$$

for the equation of $\pi_{\nu\lambda}$ in spherical polar coordinates. In addition, from Eqs. (3.1b) and (A10) we have, on $\pi_{\nu\lambda}$,

$$\omega_\lambda = \omega_\nu. \quad (\text{A15})$$

To display the geometrical character of $\pi_{\nu\lambda}$ we switch from polar coordinates ζ , ω_λ , γ_λ to Cartesian ones X_λ , Y_λ , Z_λ . Equation (A14) then becomes

$$Z_\lambda = -\cot\alpha_{\nu\lambda} X_\lambda \quad 0 \leq \gamma_\lambda \leq \pi/2 \text{ and } 3\pi/2 \leq \gamma_\lambda < 2\pi. \quad (\text{A16})$$

This is the equation of a half-plane whose edge is the Y_λ axis and which makes an angle $\pi - \alpha_{\nu\lambda}$ with the OZ_λ axis (measured counter clockwise from OZ_λ to $\pi_{\nu\lambda}$ as viewed from OY_λ).

Another quantity of considerable importance in the matching procedure is the derivative operator $\partial/\partial n_{\nu\lambda}$ normal to the surface $\pi_{\nu\lambda}$ in the direction of increasing ω_λ (Sec. IV. A). Since this surface is a half-plane, this operator is easily found by using the standard expression

$$\partial/\partial n_{\nu\lambda} = \hat{n}_{\nu\lambda} \cdot \nabla, \quad (\text{A17})$$

where $\hat{n}_{\nu\lambda}$ is a unit vector normal to $\pi_{\nu\lambda}$ in the direction of increasing ω_λ , and ∇ is the gradient operator in $X_\lambda Y_\lambda Z_\lambda$ coordinates. Expressing Eq. (A17) in the spherical polar coordinates ζ , ω_λ , and γ_λ we find

$$\begin{aligned} \frac{\partial}{\partial n_{\nu\lambda}} &= \frac{1}{\zeta} \frac{\sin\alpha_{\nu\lambda}}{\sin\omega_\lambda} \left[\left(\frac{\partial}{\partial \omega_\lambda} \right)_{\gamma_\lambda, \zeta} + \cot\alpha_{\nu\lambda} \sin\gamma_\lambda \left(\frac{\partial}{\partial \gamma_\lambda} \right)_{\omega_\lambda, \zeta} \right] \\ &= \frac{1}{\zeta} (\sin^2\alpha_{\nu\lambda} + \cos^2\alpha_{\nu\lambda} \cos^2\gamma_\lambda)^{1/2} \left[\left(\frac{\partial}{\partial \omega_\lambda} \right)_{\gamma_\lambda, \zeta} \right. \\ &\quad \left. + \cot\alpha_{\nu\lambda} \sin\gamma_\lambda \left(\frac{\partial}{\partial \gamma_\lambda} \right)_{\omega_\lambda, \zeta} \right] \\ &= \frac{1}{\zeta} \frac{\sin\alpha_{\nu\lambda}}{\sin 2\eta_\lambda} \left[\frac{1}{2} \left(\frac{\partial}{\partial \eta_\lambda} \right)_{\gamma_\lambda, \zeta} + \cot\alpha_{\nu\lambda} \sin\gamma_\lambda \left(\frac{\partial}{\partial \gamma_\lambda} \right)_{\eta_\lambda, \zeta} \right], \end{aligned} \quad (\text{A18})$$

and the indicated differentiations must be done on the full wavefunction with ζ , ω_λ (or η_λ) and γ_λ considered as independent variables before the relation between ω_λ (or η_λ) and γ_λ describing $\pi_{\nu\lambda}$ is used. The third line of Eq. (A18) results from the use of η_λ rather than ω_λ as discussed in Sec. III. B. Equation (A17) can also be evaluated in terms of ν arrangement channel coordinates, in which case we find

$$\begin{aligned} \frac{\partial}{\partial n_{\nu\lambda}} &= -\frac{1}{\zeta} \frac{\sin\alpha_{\nu\lambda}}{\sin\omega_\nu} \left[\left(\frac{\partial}{\partial \omega_\nu} \right)_{\gamma_\nu, \zeta} - \cot\alpha_{\nu\lambda} \sin\gamma_\lambda \left(\frac{\partial}{\partial \gamma_\nu} \right)_{\omega_\nu, \zeta} \right] \\ &= -\frac{1}{\zeta_\lambda} (\sin^2\alpha_{\nu\lambda} + \cos^2\alpha_{\nu\lambda} \cos^2\gamma_\lambda)^{1/2} \left[\left(\frac{\partial}{\partial \omega_\nu} \right)_{\gamma_\nu, \zeta} \right. \\ &\quad \left. - \cot\alpha_{\nu\lambda} \sin\gamma_\lambda \left(\frac{\partial}{\partial \gamma_\nu} \right)_{\omega_\nu, \zeta} \right] \\ &= -\frac{1}{\zeta} \frac{\sin\alpha_{\nu\lambda}}{\sin 2\eta_\lambda} \left[\frac{1}{2} \left(\frac{\partial}{\partial \eta_\nu} \right)_{\gamma_\nu, \zeta} - \cot\alpha_{\nu\lambda} \sin\gamma_\lambda \left(\frac{\partial}{\partial \gamma_\nu} \right)_{\eta_\nu, \zeta} \right]. \end{aligned} \quad (\text{A19})$$

APPENDIX B: EIGENVALUES OF A MATRIX OF THE FORM $\mathbf{U} = \rho^2 \mathbf{V}$

In this Appendix we show that the potential matrices in the strong interaction and matching regions [Eqs.

(3.48) and (3.61)] always have real eigenvalues even though they are not symmetric. These matrices have the general form

$$\mathbf{U} = \rho^2 \mathbf{V}, \quad (\text{B1})$$

where the real matrix ρ^2 is the matrix representation of a positive definitive operator [Eq. (3.49)] and therefore has positive real eigenvalues. \mathbf{V} is a real symmetric matrix whose eigenvalues may be positive, negative, or zero.

The first step in finding the eigenvalues of \mathbf{U} involves a diagonalization of ρ^2 ,

$$\tilde{\mathbf{K}} \rho^2 \mathbf{K} = \Lambda, \quad (\text{B2})$$

where Λ is a diagonal matrix whose elements are the (positive) eigenvalues of ρ^2 , and \mathbf{K} is the real orthogonal matrix of eigenvectors of ρ^2 . We now form the real symmetric matrix ρ by

$$\rho = \tilde{\mathbf{K}} \Lambda^{1/2} \mathbf{K}, \quad (\text{B3})$$

where the diagonal matrix $\Lambda^{1/2}$ has diagonal elements which are the square roots of those of Λ . ρ behaves as if it were the "square root" of ρ^2 in many applications, since, from Eqs. (B2) and (B3),

$$\rho \rho = \rho^2. \quad (\text{B4})$$

Next, we define the real matrix \mathbf{W} as

$$\mathbf{W} = \rho^{-1} \mathbf{U} \rho = \rho \mathbf{V} \rho, \quad (\text{B5})$$

where the second equality in Eq. (B5) follows from Eq. (B1). From Eq. (B5), it is obvious that \mathbf{W} is real symmetric, and it may therefore be diagonalized by a real

orthogonal matrix which we denote by \mathbf{T} :

$$\tilde{\mathbf{T}} \mathbf{W} \mathbf{T} = \mathbf{E}. \quad (\text{B6})$$

The diagonal matrix \mathbf{E} contains the real eigenvalues of \mathbf{W} .

Finally, if we define the nonorthogonal, nonsymmetric, but real matrix \mathbf{S} by

$$\mathbf{S} = \rho \mathbf{T}, \quad (\text{B7})$$

we obtain, from Eqs. (B5) and (B6),

$$\mathbf{S}^{-1} \mathbf{U} \mathbf{S} = \mathbf{E}, \quad (\text{B8})$$

which proves that the matrix \mathbf{S} diagonalizes \mathbf{U} with the resulting real eigenvalues contained in \mathbf{E} .

APPENDIX C: RELATIONS BETWEEN DISTINGUISHABLE ATOM SCATTERING AMPLITUDES FOR ATOM-DIATOM REACTIONS INVOLVING HOMONUCLEAR DIATOMIC MOLECULES

In this Appendix we investigate the consequences of two-atom permutational symmetry (as discussed in Sec. VI. A) on the distinguishable-atom scattering amplitudes. We show that in collisions for which Eq. (6.1) is valid (i. e., collisions of an atom with a homonuclear diatomic molecule), the resultant scattering amplitudes $f_{\lambda\nu j}^{\nu\nu'j'}$ and $f_{\lambda\nu j}^{\kappa\nu'j'}$ are related by Eq. (6.3) and that $f_{\lambda\nu j}^{\nu\nu'j'}$ obeys Eq. (6.4). [The circumflex on \hat{f} of Eq. (5.28) will be omitted in this Appendix.]

We first rewrite the asymptotic behavior of the scattering solution Eq. (5.23) as

$$\begin{aligned} \Psi^{\lambda\nu j\lambda}[P] &\underset{R_\lambda \rightarrow \infty}{\sim} e^{ik_{\lambda\nu}^{\lambda} R_\lambda \cos \theta_\lambda} \phi_{j_\lambda}(\theta_{r_\lambda}) \frac{\phi_{\nu\lambda}^{\lambda}(r_\lambda)}{r_\lambda^{1/2}} + \sum_{\nu' j'_\lambda} \frac{e^{ik_{\lambda\nu'}^{\lambda} R_\lambda}}{R_\lambda^{1/2}} f_{\lambda\nu' j'_\lambda}^{\nu\nu' j'_\lambda}(\theta_\lambda) \phi_{j'_\lambda}(\theta_{r_\lambda}) \frac{\phi_{\nu\lambda}^{\lambda}(r_\lambda)}{r_\lambda^{1/2}} \left(\frac{\hbar}{\mu |V_{\nu\lambda}^{\lambda}|} \right)^{1/2} \\ &\underset{R_\nu \rightarrow \infty}{\sim} \sum_{\nu' j'_\nu} \frac{e^{ik_{\nu\nu'}^{\nu} R_\nu}}{R_\nu^{1/2}} f_{\lambda\nu' j'_\nu}^{\nu\nu' j'_\nu}(\theta_\nu) \phi_{j'_\nu}(\theta_{r_\nu}) \frac{\phi_{\nu\nu}^{\nu}(r_\nu)}{r_\nu^{1/2}} \left(\frac{\hbar}{\mu |V_{\nu\nu}^{\nu}|} \right)^{1/2} \\ &\underset{R_\kappa \rightarrow \infty}{\sim} \sum_{\nu' j'_\kappa} \frac{e^{ik_{\kappa\nu'}^{\kappa} R_\kappa}}{R_\kappa^{1/2}} f_{\lambda\nu' j'_\kappa}^{\kappa\nu' j'_\kappa}(\theta_\kappa) \phi_{j'_\kappa}(\theta_{r_\kappa}) \frac{\phi_{\nu\kappa}^{\kappa}(r_\kappa)}{r_\kappa^{1/2}} \left(\frac{\hbar}{\mu |V_{\nu\kappa}^{\kappa}|} \right)^{1/2}. \end{aligned} \quad (\text{C1})$$

If the diatomic target in the incident channel is homonuclear, the physical system should be invariant to the operator $P_{\nu\kappa}$ which interchanges the two identical atoms A_ν and A_κ involved. If we perform this interchange, the coordinates which define the system in each arrangement channel become (by inspection of Fig. 1)

$$(R_\lambda, r_\lambda) \rightarrow (R_\lambda, -r_\lambda), \quad (R_\nu, r_\nu) \rightarrow (R_\kappa, -r_\kappa), \quad (R_\kappa, r_\kappa) \rightarrow (R_\nu, -r_\nu), \quad (\text{C2})$$

which is equivalent to

$$\begin{aligned} (R_\lambda, \theta_\lambda) &\rightarrow (R_\lambda, \theta_\lambda), & (r_\lambda, \theta_{r_\lambda}) &\rightarrow (r_\lambda, \theta_{r_\lambda} + \pi), & (R_\nu, \theta_\nu) &\rightarrow (R_\kappa, \theta_\kappa), \\ (r_\nu, \theta_{r_\nu}) &\rightarrow (r_\kappa, \theta_{r_\kappa} + \pi), & (R_\kappa, \theta_\kappa) &\rightarrow (R_\nu, \theta_\nu), & (r_\kappa, \theta_{r_\kappa}) &\rightarrow (r_\nu, \theta_{r_\nu} + \pi). \end{aligned}$$

If we make these substitutions into Eq. (C1) realizing that $\phi_{j_\lambda}(\theta_{r_\lambda} + \pi) = (-1)^{j_\lambda} \phi_{j_\lambda}(\theta_{r_\lambda})$, and appropriately relabel the quantum numbers which serve as summation indices, we obtain

$$\begin{aligned} P_{\nu\kappa} \Psi^{\lambda\nu j\lambda}[P] &\underset{R_\lambda \rightarrow \infty}{\sim} (-1)^{j_\lambda} e^{ik_{\lambda\nu}^{\lambda} R_\lambda \cos \theta_\lambda} \phi_{j_\lambda}(\theta_{r_\lambda}) \frac{\phi_{\nu\lambda}^{\lambda}(r_\lambda)}{r_\lambda^{1/2}} + \sum_{\nu' j'_\lambda} (-1)^{j'_\lambda} \frac{e^{ik_{\lambda\nu'}^{\lambda} R_\lambda}}{R_\lambda^{1/2}} f_{\lambda\nu' j'_\lambda}^{\nu\nu' j'_\lambda}(\theta_\lambda) \phi_{j'_\lambda}(\theta_{r_\lambda}) \frac{\phi_{\nu\lambda}^{\lambda}(r_\lambda)}{r_\lambda^{1/2}} \left(\frac{\hbar}{\mu |V_{\nu\lambda}^{\lambda}|} \right)^{1/2} \\ &\underset{R_\kappa \rightarrow \infty}{\sim} \sum_{\nu' j'_\kappa} (-1)^{j'_\kappa} \frac{e^{ik_{\kappa\nu'}^{\kappa} R_\kappa}}{R_\kappa^{1/2}} f_{\lambda\nu' j'_\kappa}^{\kappa\nu' j'_\kappa}(\theta_\kappa) \phi_{j'_\kappa}(\theta_{r_\kappa}) \frac{\phi_{\nu\kappa}^{\kappa}(r_\kappa)}{r_\kappa^{1/2}} \left(\frac{\hbar}{\mu |V_{\nu\kappa}^{\kappa}|} \right)^{1/2} \\ &\underset{R_\nu \rightarrow \infty}{\sim} \sum_{\nu' j'_\nu} (-1)^{j'_\nu} \frac{e^{ik_{\nu\nu'}^{\nu} R_\nu}}{R_\nu^{1/2}} f_{\lambda\nu' j'_\nu}^{\nu\nu' j'_\nu}(\theta_\nu) \phi_{j'_\nu}(\theta_{r_\nu}) \frac{\phi_{\nu\nu}^{\nu}(r_\nu)}{r_\nu^{1/2}} \left(\frac{\hbar}{\mu |V_{\nu\nu}^{\nu}|} \right)^{1/2}. \end{aligned} \quad (\text{C3})$$

The line-wave part of (C3) differs only by a factor of $(-1)^j$ from the corresponding part of (C1). Since the scattering solutions are unique (except for a normalization constant), this implies that this proportionality relation must hold over the entire configuration space, i. e., that

$$P_{\nu\kappa}\psi^{\lambda\nu j\lambda}[P] = (-1)^j\lambda\psi^{\lambda\nu j\lambda}[P] \quad (\text{C4})$$

everywhere. Replacement of Eqs. (C1) and (C3) into (C4) and identification of the corresponding outgoing wave parts in channel λ immediately yields

$$f_{\lambda\nu\lambda}^{\lambda\nu j\lambda} = (-1)^j\lambda + j\lambda f_{\lambda\nu\lambda}^{\lambda\nu j\lambda}, \quad (\text{C5})$$

which is equivalent to Eq. (6.4). In order to compare the outgoing wave solutions in channels ν and κ , we first must realize that the $\phi_{\nu\kappa}^{\nu}(r_\kappa)$ (and $k_{\nu\kappa}^{\nu}$) of Eq. (C3), and the $\phi_{\nu\kappa}^{\kappa}(r_\kappa)$ (and $k_{\nu\kappa}^{\kappa}$) of Eq. (C1) are identical since these represent vibrational wavefunctions in the two product arrangement channels $A_\kappa A_\lambda$ and $A_\lambda A_\nu$, both of which are the same for a homonuclear target $A_\nu A_\kappa$. This allows us to compare the outgoing wave solutions in channels ν and κ in Eq. (C4), obtaining

$$f_{\lambda\nu\lambda}^{\nu\nu j\kappa} = (-1)^j\lambda + j\kappa f_{\lambda\nu\lambda}^{\kappa\nu j\kappa} \quad (\text{C6})$$

in both cases. Equation (C6) is identical to Eq. (6.3).

If atoms A_λ and A_ν are identical, a derivation similar to that of (C4) leads to

$$P_{\lambda\nu}\psi^{\lambda\nu j\lambda}[P] = (-1)^j\lambda\psi^{\nu\nu j\lambda}[P], \quad (\text{C7})$$

and if A_λ and A_κ are identical we get

$$P_{\lambda\kappa}\psi^{\lambda\nu j\lambda}[P] = (-1)^j\lambda\psi^{\kappa\nu j\lambda}[P]. \quad (\text{C8})$$

From Eq. (C7) results

$$f_{\lambda\nu\lambda}^{\nu\nu j\nu} = (-1)^j\lambda + j\nu f_{\lambda\nu\lambda}^{\lambda\nu j\nu}, \quad (\text{C9})$$

$$f_{\lambda\nu\lambda}^{\lambda\nu j\nu} = (-1)^j\lambda + j\nu f_{\lambda\nu\lambda}^{\nu\nu j\nu}, \quad (\text{C10})$$

$$f_{\lambda\nu\lambda}^{\kappa\nu j\kappa} = (-1)^j\lambda + j\kappa f_{\lambda\nu\lambda}^{\kappa\nu j\kappa}, \quad (\text{C11})$$

and analogous expressions stem from Eq. (C8):

$$f_{\lambda\nu\lambda}^{\kappa\nu j\kappa} = (-1)^j\lambda + j\kappa f_{\lambda\nu\lambda}^{\lambda\nu j\kappa}, \quad (\text{C12})$$

$$f_{\lambda\nu\lambda}^{\lambda\nu j\kappa} = (-1)^j\lambda + j\kappa f_{\lambda\nu\lambda}^{\kappa\nu j\kappa}, \quad (\text{C13})$$

$$f_{\lambda\nu\lambda}^{\nu\nu j\nu} = (-1)^j\lambda + j\nu f_{\lambda\nu\lambda}^{\lambda\nu j\nu}, \quad (\text{C14})$$

If all three atoms are identical, Eqs. (C4)–(C14) are all valid, as well as expressions resulting from cyclic permutations of indices λ , ν , κ .

For reactions in three dimensions, Eqs. (C2) are still valid. The rotational diatomic wavefunctions $\phi_{j\lambda}(\theta_{r_\lambda})$ are replaced by the spherical harmonics $Y_{j\lambda m_{j\lambda}}(\theta_{r_\lambda}, \phi_{r_\lambda})$, where θ_{r_λ} , ϕ_{r_λ} are the spherical polar angles of r_λ , and j_λ , $m_{j\lambda}$ are the diatom's angular momentum quantum numbers. Replacement of r_λ by $-r_\lambda$ is equivalent to replacing those polar angles by $\pi - \theta_{r_\lambda}$ and $\phi_{r_\lambda} + \pi$, respectively. The relation $Y_{j\lambda m_{j\lambda}}(\pi - \theta_{r_\lambda}, \phi_{r_\lambda} + \pi) = (-1)^{j_\lambda} \times Y_{j\lambda m_{j\lambda}}(\theta_{r_\lambda}, \phi_{r_\lambda})$, which is analogous to the relation $\phi_{j\lambda}(\theta_{r_\lambda} + \pi) = (-1)^{j_\lambda} \phi_{j\lambda}(\theta_{r_\lambda})$ used to derive Eq. (C4). As a result, that equation, as well as Eqs. (C5)–(C14) are also valid in three dimensions, as long as the quantum numbers $v_{j\lambda}$ (and their ν and κ counterparts) are augmented by the diatomic rotational angular momentum projection quantum number $m_{j\lambda}$.

APPENDIX D: POSTANTISYMMETRIZATION FOR THE H + H₂ EXCHANGE REACTION

Although correct expressions for the indistinguishable (antisymmetrized) cross sections in terms of the distinguishable atom reactive and nonreactive amplitudes have been listed by Doll, George, and Miller,⁴⁴ who have obtained their results using the integrodifferential equation approach described by Miller,⁴⁵ there seems to be confusion in the use of these expressions so we shall derive them here in order to clarify their meanings. We will follow the postantisymmetrization procedure outlined by Schiff²³ which is somewhat more transparent than Miller's. In all of our treatment below we assume that the interaction potential is not spin dependent and that there are no external magnetic fields present.

We start by rewriting the asymptotic physical solution [Eq. (5.23)] for distinguishable-atom scattering (in the mass-scaled coordinate system). To simplify the notation we omit the symbol $[P]$ (which will be implied throughout this Appendix) and replace the labels (α, β, γ) by $(1, 2, 3)$. Therefore, (λ, ν, κ) will stand for one of the cyclic permutations $(1, 2, 3)$, $(2, 3, 1)$, and $(3, 1, 2)$. Choosing the first of these we get

$$\begin{aligned} \Psi^{1\nu j_1}(1, 2, 3) &\underset{R_1 \rightarrow \infty}{\sim} e^{ik_{1j_1}^1 \cdot \mathbf{R}_1} W_{v_1 j_1}^1(2, 3) \\ &+ \sum_{v_1' j_1'} \frac{e^{ik_{v_1' j_1'}^1 R_1}}{R_1^{1/2}} W_{v_1' j_1'}^1(2, 3) C_1^{v_1' j_1'} \hat{f}_{1\nu_1 j_1}^{1\nu_1 j_1}(\theta_1) \\ &\underset{R_2 \rightarrow \infty}{\sim} \sum_{v_2 j_2} \frac{e^{ik_{v_2 j_2}^2 R_2}}{R_2^{1/2}} W_{v_2 j_2}^2(3, 1) C_2^{v_2 j_2} \hat{f}_{2\nu_2 j_2}^{2\nu_2 j_2}(\theta_2) \\ &\underset{R_3 \rightarrow \infty}{\sim} \sum_{v_3 j_3} \frac{e^{ik_{v_3 j_3}^3 R_3}}{R_3^{1/2}} W_{v_3 j_3}^3(1, 2) C_3^{v_3 j_3} \hat{f}_{3\nu_3 j_3}^{3\nu_3 j_3}(\theta_3), \end{aligned} \quad (\text{D1})$$

where

$$W_{\lambda j_\lambda}^\lambda(\nu, \kappa) = \frac{\phi_{j_\lambda}^\lambda(\theta_{r_\lambda}) \phi_{j_\lambda}^\lambda(r_\lambda)}{r_\lambda^{1/2}} \quad (\text{D2})$$

$$C_\lambda^{v_\lambda j_\lambda} = \left(\frac{\hbar}{\mu |V_{\lambda j_\lambda}^\lambda|} \right)^{1/2} \quad (\text{D3})$$

Note that we have used the numbers 1, 2, and 3 as both an arrangement channel label and a particle label. Provided that we always permute particles in a cyclic way in our arrangement channel labeling, the two designations are identical and we will consider this to be the case here. This means that the coordinate r_1 is the internuclear vector from particle 2 to particle 3 (in the $\mathbf{R}_1, \mathbf{r}_1$ coordinate system), and therefore the 2, 3 diatomic molecule wavefunction is a function of r_1 . For H + H₂, the separated arrangement channel quantum states are all identical, so the labels $v_1 j_1$, $v_2 j_2$, and $v_3 j_3$ are essentially dummy indices and do not imply, for example, that $W_{v_1 j_1}^1$ differs in its functional form from $W_{v_2 j_2}^2$ or $W_{v_3 j_3}^3$ when $j_1 = j_2 = j_3$ and $v_1 = v_2 = v_3$. As a result, we may drop the subscripts λ of the quantum numbers $v_\lambda j_\lambda$ and the constants C_λ as well as the superscript in the W , k , and V . Using Eq. (C4) for the cyclic permutation $(\lambda, \nu, \kappa) = (1, 2, 3)$, we get

$$P_{23}\Psi^{1\nu j}(1, 3, 2) = \Psi^{1\nu j}(1, 2, 3) = (-1)^j \Psi^{1\nu j}(1, 3, 2), \quad (\text{D4a})$$

TABLE I. Antisymmetrized scattering amplitudes $\hat{f}_{ij}^{(k)vv'j'}$ and their relation to the distinguishable atom amplitudes $\hat{f}_{1vj}^{1v'j'}$ and $\hat{f}_{2vj}^{2v'j'}$.^a

Initial state i	j	final state j'	k	1	2	3	4	5	6	7	8
				Odd	Odd	Odd	Odd	Odd	Odd	Even	Even
				ortho	ortho	ortho	ortho	ortho	ortho	para	para
1	Odd	ortho	$\hat{f}_1^1 + \hat{f}_2^1$	0	0	0	0	0	0	0	0
2	Odd	ortho	0	\hat{f}_1^1	$\sqrt{2}\hat{f}_2^1$	0	0	0	0	$\sqrt{2}\hat{f}_2^1$	0
3	Odd	ortho	0	$\sqrt{2}\hat{f}_2^1$	$\hat{f}_1^1 + \hat{f}_2^1$	0	0	0	0	$-\hat{f}_2^1$	0
4	Odd	ortho	0	0	0	$\hat{f}_1^1 + \hat{f}_2^1$	$\sqrt{2}\hat{f}_2^1$	0	0	0	\hat{f}_2^1
5	Odd	ortho	0	0	0	$\sqrt{2}\hat{f}_2^1$	\hat{f}_1^1	0	0	0	$-\sqrt{2}\hat{f}_2^1$
6	Odd	ortho	0	0	0	0	0	$\hat{f}_1^1 + 2\hat{f}_2^1$	0	0	0
7	Even	para	0	$-\sqrt{2}\hat{f}_2^1$	\hat{f}_2^1	0	0	0	0	$\hat{f}_1^1 - \hat{f}_2^1$	0
8	Even	para	0	0	0	$-\hat{f}_2^1$	$\sqrt{2}\hat{f}_2^1$	0	0	0	$\hat{f}_1^1 - \hat{f}_2^1$

^aThe indices vj and $v'j'$ on the $\hat{f}_{1vj}^{1v'j'}$ and $\hat{f}_{2vj}^{2v'j'}$ are omitted.

which is valid in all of configuration space. In addition, using the cyclic permutation $(\lambda, \nu, \kappa) = (2, 3, 1)$, Eq. (C7) furnishes

$$P_{23}\Psi^{2vj}(2, 3, 1) = (-1)^j\Psi^{3vj}(3, 1, 2). \quad (\text{D4b})$$

Let us now consider the spin wavefunctions of the separated atom plus diatom system in arrangement channel 1. Since the three hydrogen atoms have spin $\frac{1}{2}$, there are eight such wavefunctions which can be chosen to be

$$v_1(1, 2, 3) = \alpha(1)\alpha(2)\alpha(3), \quad (\text{D5a})$$

$$v_2(1, 2, 3) = \beta(1)\alpha(2)\alpha(3), \quad (\text{D5b})$$

$$v_3(1, 2, 3) = \frac{1}{\sqrt{2}}\alpha(1)[\alpha(2)\beta(3) + \beta(2)\alpha(3)], \quad (\text{D5c})$$

$$v_4(1, 2, 3) = \frac{1}{\sqrt{2}}\beta(1)[\alpha(2)\beta(3) + \beta(2)\alpha(3)], \quad (\text{D5d})$$

$$v_5(1, 2, 3) = \alpha(1)\beta(2)\beta(3), \quad (\text{D5e})$$

$$v_6(1, 2, 3) = \beta(1)\beta(2)\beta(3), \quad (\text{D5f})$$

$$v_7(1, 2, 3) = \frac{1}{\sqrt{2}}\alpha(1)[\alpha(2)\beta(3) - \beta(2)\alpha(3)], \quad (\text{D5g})$$

$$v_8(1, 2, 3) = \frac{1}{\sqrt{2}}\beta(1)[\alpha(2)\beta(3) - \beta(2)\alpha(3)]. \quad (\text{D5h})$$

They are orthonormal eigenfunctions of S_z but not of S^2 and have the symmetry property

$$v_i(1, 3, 2) = \begin{cases} v_i(1, 2, 3) & i = 1-6 \\ -v_i(1, 2, 3) & i = 7, 8. \end{cases} \quad (\text{D6})$$

The total separated atom plus diatom wavefunctions (including space and spin coordinates) are then

$$\Phi^{1vj(i)}(1, 2, 3) = \Psi^{1vj}(1, 2, 3)v_i(1, 2, 3) \quad i = 1-8, \quad (\text{D7})$$

where (i) designates the spin state of the system. Since $\Phi^{1vj}(1, 2, 3)$ must be antisymmetric with respect to permutation of particles 2 and 3, we have the requirements [in view of Eqs. (D4) and (D6)] that

$$j = \begin{cases} \text{odd for } i = 1-6 \text{ (ortho states)} \\ \text{even for } i = 7, 8 \text{ (para states)}. \end{cases} \quad (\text{D8})$$

We now form the completely antisymmetric wavefunction $\Psi^{Avj(i)}(1, 2, 3)$ by taking the symmetric linear combination of the partly antisymmetric wavefunctions $\Phi^{1vj}(\lambda\nu\kappa)$ for the three cyclic permutations of $(1, 2, 3)$ having the same initial vj :

$$\Psi^{Avj(i)} = \Phi^{1vj(i)}(1, 2, 3) + \Phi^{2vj(i)}(2, 3, 1) + \Phi^{3vj(i)}(3, 1, 2) \quad i = 1-8. \quad (\text{D9})$$

Equations (D4), (D6), and (D8) can be used to prove that $\Psi^{Avj(i)}$ is antisymmetric under a permutation of any two of the three particles in the system. This then is the correct scattering solution, and its asymptotic behavior can be used to determine the correct antisymmetrized scattering amplitudes. This asymptotic behavior can be determined by evaluating $\Psi^{Avj(i)}$ at large values of R_1 (or R_2 or R_3), which yields

$$\begin{aligned} \Psi^{Avj(i)}(1, 2, 3) \sim_{R_1 \rightarrow \infty} & e^{ik_{vj} \cdot \mathbf{R}_1} W_{vj}(2, 3) v_i(1, 2, 3) \\ & + \sum_{v'j'} \frac{e^{ik_{v'j'} \cdot \mathbf{R}_1}}{R_1^{1/2}} W_{v'j'}^1(2, 3) C^{v'j'} (\hat{f}_{1vj}^{1v'j'} v_i(1, 2, 3) + \hat{f}_{2vj}^{2v'j'} v_i(2, 3, 1) + \hat{f}_{3vj}^{3v'j'} v_i(3, 1, 2)). \end{aligned} \quad (\text{D10})$$

This has the form of a physical scattering solution, but the expression in large parentheses must be re-expressed in terms of the $v_k(1, 2, 3)$ spin functions of the final separated atom-diatom ($k=1-8$). Accordingly, we write

$$\hat{f}_{1vj}^{1v'j'} v_i(1, 2, 3) + \hat{f}_{2vj}^{1v'j'} v_i(2, 3, 1) + \hat{f}_{3vj}^{1v'j'} v_i(3, 1, 2) \\ = \sum_{k=1}^8 f_{(i)vj}^{A(k)v'j'} v_k(1, 2, 3), \quad (D11)$$

where $f_{(i)vj}^{A(k)v'j'}$ is the antisymmetrized scattering amplitude for scattering from initial state $(i)vj$ (spin state i) to final state $(k)v'j'$ [where Eq. (D8) must be satisfied for both of these states]. We can solve for the $f_{(i)vj}^{A(k)v'j'}$ by multiplying Eq. (D11) by $v_i(1, 2, 3)$, integrating over all spin variables and then replacing the index i by k in the result. The resulting expressions for $f_{(i)vj}^{A(k)v'j'}$ in terms of the distinguishable-atom scattering amplitudes are given in Table I. The expressions in that table have been simplified by the use of the relation [see Eqs. (6.3)]:

$$\hat{f}_{2vj}^{1v'j'} = (-1)^{j+j'} \hat{f}_{3vj}^{1v'j'}. \quad (D12)$$

In the notation of Doll, George, and Miller,⁴⁴ $\hat{f}_{1vj}^{1v'j'}$ is the direct while $\hat{f}_{2vj}^{1v'j'}$ is the exchange scattering amplitude.

The state-to-state cross sections are [from Eq. (5.24)]

$$\sigma_{(i)vj}^{(j)v'j'} = \frac{1}{k_{vj}} |\hat{f}_{(i)vj}^{(j)v'j'}|^2, \quad (D13)$$

and the cross sections of Eq. (6.5) are obtained by summing Eq. (D13) over final spin states and averaging over initial ones. As an example, the para-to-ortho cross section [Eq. (6.5b)] is given by (dropping the $vj, v'j'$ indices but retaining the spin labels)

$$\sigma_p^o = \frac{1}{2} (\sigma_7^1 + \sigma_7^2 + \sigma_7^3 + \sigma_7^4 + \sigma_7^5 + \sigma_7^6 + \sigma_8^1 + \sigma_8^2 + \sigma_8^3 + \sigma_8^4 + \sigma_8^5 + \sigma_8^6) \\ = \frac{3}{k} |\hat{f}_2^1|^2. \quad (D14)$$

The derivation of the antisymmetrized scattering amplitudes of Table I was based on the validity of Eqs. (D4) and (D6). The latter comes from the properties of the spin states of Eq. (D5) which are the correct ones for the three-dimensional world. Equations (D4a) and (D4b) came from Eqs. (C4) and (C7), respectively, which as pointed out at the end of Appendix C, are also valid in three dimensions after including the projection quantum numbers m_j . The other characteristics of Eq. (D1) which change in going from 2D to 3D are irrelevant for the derivation of the antisymmetrized scattering amplitudes. As a result, the formulas of Table I are also valid in three dimensions when augmented by the quantum numbers m_j . A similar statement is valid for Eqs. (6.5) if k_{vj}^λ is replaced by $(k_{vj}^\lambda)^2$.

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many others, but they do not display all of the convenient properties of the coordinates of Eq. (2.2).

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²⁹The angles θ_ν and θ_λ differ by an angle $\Delta_{\nu\lambda}$ which is a function of r_λ , R_λ , and γ_λ only as seen in Eqs. (A8) and (A9). In addition, Eqs. (A7) show that γ_ν also depends on those three variables only. Therefore, $\varphi_J(\theta_\lambda)$ is also an eigenfunction of $\hbar/i(\partial/\partial\theta_\nu)$, with the same eigenvalue $J\hbar$. The quantum number J is, as a result, independent of the arrangement channel λ used to obtain it.

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There will, in general, be N of these kinds of scattering solutions which are linearly independent (for a coupled-channel expansion truncated at N terms in each arrangement channel), along with N having incoming waves in channel ν and N with incoming waves in channel κ for a total of $3N$ solutions. The latter two sets of solutions will have only outgoing waves in channel λ and, in the absence of the inclusion of dissociated states, it will be impossible to linearly combine these latter $2N$ solutions to generate the N sets of solutions which have incoming waves in channel λ . Therefore we have $3N$ scattering solutions which are linearly independent when the entire configuration space is considered, although only $2N$ of them are independent in any one asymptotic arrangement channel.

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